

Fundamentals in Organic Geochemistry

Jan Schwarzbauer
Branimir Jovančević

Organic Pollutants in the Geosphere



Springer

Fundamentals in Organic Geochemistry

Series editors

Jan Schwarzbauer

RWTH Aachen University, Aachen, Germany

Branimir Jovančičević

University of Belgrade, Belgrade, Serbia

Organic Geochemistry is a modern scientific subject characterized by a high transdisciplinarity and located at the edge of chemistry, environmental sciences, geology and biology. Therefore, there is a need for a flexible offer of appropriate academic teaching material (BSc and MSc level) addressed to the variety of students coming originally from different study disciplines. For such a flexible usage the textbook series 'Fundamentals in Organic Geochemistry' consists of different volumes with clear defined aspects and with manageable length. Students as well as lecturers will be able to choose those organic-geochemical topics that are relevant for their individual studies and programs. Hereby, it is the intention to introduce (i) clearly structured and comprehensible knowledge, (ii) process orientated learning and (iii) the complexity of natural geochemical systems. This textbook series covers different aspects of Organic Geochemistry comprising e.g. diagenetic pathways from biomolecules to molecular fossils, the chemical characterization of fossil matter, organic geochemistry in environmental sciences, and applied analytical aspects.

More information about this series at <http://www.springer.com/series/13411>

Jan Schwarzbauer • Branimir Jovančičević

Organic Pollutants in the Geosphere

 Springer

Jan Schwarzbauer
RWTH Aachen University
Aachen, Nordrhein-Westfalen, Germany

Branimir Jovančičević
University of Belgrade
Belgrade, Serbia

ISSN 2199-8647 ISSN 2199-8655 (electronic)
Fundamentals in Organic Geochemistry
ISBN 978-3-319-68937-1 ISBN 978-3-319-68938-8 (eBook)
<https://doi.org/10.1007/978-3-319-68938-8>

Library of Congress Control Number: 2017958158

© Springer International Publishing AG 2018

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Printed on acid-free paper

This Springer imprint is published by Springer Nature
The registered company is Springer International Publishing AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Preface

Organic geochemistry is a highly diverse scientific field with a lot of complementary aspects from different disciplines. For students, this complexity might be confusing at the beginning. Therefore, this book series will help to get familiar with basic aspects of *organic geochemistry* bit by bit.

The first two volumes (*Fossil Matter in the Geosphere* and *From Biomolecules to Chemofossils*) focused on the geochemistry of natural organic matter over geological time periods. However, humans have substantially influenced the environment on a much shorter time scale. A dominant impact is attributed to the production, use and discharge of man-made substances with harmful effects. And these pollutants include numerous organic compounds. Hence, in this volume, many representative organic pollutants are introduced with respect to their chemical properties, their specific risk potentials and their appearance in the environment (Chap. 2). At first, a general introduction to the main processes affecting the environmental fate and risk of organic contaminants is given in Chap. 1 comprising the general aspect of dispersion, toxicity and degradation. In the last chapters, some specific organic contaminations and approaches are discussed in more detail.

Comparable to the second issue of this book series, this textbook is based on BSc-/MSc-level lectures that are part of the geoscientific and geochemical education at RWTH Aachen University and the University of Belgrade. Principally, this volume aims at supporting students to get familiar with the basic aspects and fundamental processes related to the *organic geochemistry* of anthropogenic pollutants.

Aachen, Germany
Belgrade, Serbia

Jan Schwarzbauer
Branimir Jovančičević

Contents

1	Fate and Assessment of Organic Pollutants in the Geosphere.....	1
1.1	Environmental Dispersion and Distribution	3
1.2	Toxicological Assessment.....	15
1.3	Transformation and Degradation	28
1.4	Organic Pollution in Hydro-, Pedo- and Atmosphere.....	41
1.5	Bound Residues	47
	References.....	54
2	Organic Pollutants	55
2.1	Halogenated Compounds.....	55
2.1.1	Halogenated Aliphatics	60
2.1.2	Halogenated Aromatics.....	65
2.2	Pesticides	81
2.3	Pharmaceuticals	93
2.4	Personal Care Products	102
2.4.1	Softening Agents.....	104
2.4.2	Surfactants	105
2.4.3	Fragrances.....	113
2.4.4	Miscellaneous Ingredients	118
2.5	Plasticizers and Further Technical Additives	119
2.6	Explosives	124
2.7	Aromatic Hydrocarbons – PAH and BTEX.....	127
2.8	Organometallics	138
2.8.1	Methylated Mercury Species	140
2.8.2	Butyl Tin Compounds.....	143
	References.....	150
3	Petrogenic Contaminations	157
	References.....	167

4 POPs – A Special Perspective on a Specific Group of Contaminants..... 169

Reference 173

5 Anthropogenic Marker..... 175

References..... 185

Chapter 1

Fate and Assessment of Organic Pollutants in the Geosphere

Outlook

For risk assessments of organic pollutants three major properties and processes are relevant: dispersion, environmental stability and (eco)toxicological effects. Beside a brief introduction of these parameters and their application, also two further topics comprising the formation of bound residues as well as specific environmental aspects in the three main compartments hydro-, atmo- and pedosphere are discussed.

Keywords Environmental fate • Risk assessment • Priority pollutants • REACH • PBT criteria

For risk assessments of organic pollutants three major properties and processes are relevant: dispersion, environmental stability and (eco)toxicological effects. Beside a brief introduction of these parameters and their application, also two further topics comprising the formation of bound residues as well as specific environmental aspects in the three main compartments hydro-, atmo- and pedosphere are discussed.

All organisms are involved in the global cycles of compounds and elements (e.g. carbon cycle, cycle of heavy metals). With respect to organic substances, organisms take up and secrete individual compounds and they transform and degrade them, but they also build up new organics. Noteworthy, humans started at a certain point in history to influence the natural matter in a way that they unbalance the so far stable natural cycles of materials.

Beside an excessive usage of natural matter as a result of a drastically increasing population, the synthesis of so far naturally not existing compounds, so-called xenobiotics, marks a radical point in human impact on nature. This development is closely related to the period of industrialisation starting in the mid nineteenth century. Till now thousands to millions of new substances have been synthesized and have partly been released to the environment as the result of human usage and disposal. This includes common groups of products used in our daily life such as personal care products, pharmaceuticals or plastics. More specific applications e.g. in agriculture (pesticides, fertilisers etc.), in industry (solvents, intermediates in synthesis, catalysts,

Table 1.1 Criteria for the assessment of substances according to REACH

Criteria	PBT (persistent, bioaccumulative, toxic)	vPvB (very persistent, very bio-accumulative)
Persistence	<u>Half-life period</u>	<u>Half-life period</u>
	Sea water: > 60 d	Water: > 60 d
	Fresh water: > 40 d	Sediment: > 180 d
	Marine sediment: > 180 d	Soil: > 180 d
	Limnic sediment: > 120 d	
	Soil: > 120 d	
Bioaccumulation	BFC > 2000	BFC > 5000
Toxicity	NOEC > 0.01 mg/l	
	CMT	
	Toxicity T, R48 or Xn	

combustion products etc.) or for military purposes (explosives, gasoline etc.) cause dramatic anthropogenic emissions of organic pollutants into the environment as well.

Noteworthy, these areas of human activities also effect the occurrence and distribution of heavy metals, radionuclides (including artificially generated radioisotopes) or nutrients. However, in this book the focus lies on the chemical characterisation, environmental fate and assessment of *organic* pollutants produced, consumed and discharged by humans.

Prior to introducing the chemical characterisation and environmental impact of individual substances or compound groups (see Chap. 2), a brief introduction into those parameters or properties commonly used for assessing the environmental relevance of pollutants will be discussed. In general, this comprises three aspects: the distribution and dispersion of pollutants on a local/regional but more important on a global and long-term scale, their (eco)toxicological effects and their environmental stability.

The relevance and application of these parameters for assessing the potential environmental risk of compounds is nicely illustrated by the current European regulation for chemicals: REACH (**R**egistration, **E**valuation, **A**uthorisation and **R**estriction of **C**hemicals; Reg. (EC) No 1907/2006). In Table 1.1 the criteria applicable for evaluation of chemicals are summarized. These criteria represent the three already mentioned aspects covering (eco)toxicity, environmental stability and preferred occurrence.

With respect to the protection of ecosystems, similar systematic concepts have been applied for identifying environmentally relevant pollutants. Identification and selection of substances with an elevated risk to harm the environment lead to lists of so-called priority pollutants, marking compounds that are suspicious in terms of (eco)toxicity, environmental stability or accumulation tendencies and that need to be monitored. An example is the European Water Framework Directive (Directive 2000/60/EC), that contains a list of priority pollutants with harmful properties for ground and surface water systems. The selection is based on the complementary application of parameters covering the three main parameters mentioned before. Also further approaches established for protecting ecosystems used such lists as bases for monitoring measures (e.g. by the US EPA or the European Union). Noteworthy, lists of priority pollutants are often dominated by organic pollutants as exemplified in Table 1.2.

Table 1.2 Lists of priority pollutants in different legal regulations

Priority pollutant lists	US EPA (2014)	Annex 1 of EU Water Framework Directive (2008)	Canadian Environmental Protection Act, 1st list (1989)
Number of substances	127	33	44
Proportion of organic pollutants	Ca. 88%	Ca. 88%	Ca. 84%
Examples of organic pollutants listed	Heptachlor	Diuron	Tetrachloro ethylene
	Vinylchloride	Dichloromethane	Toluene
	Fluorene	Nonylphenols	Styrene
	HCHs	Benzo(a)pyrene	Benzidine
	DDT	Tributyl tin	Hexachlorobenzene
	Benzene	Trichlorobenzenes	Methyl metacrylate
	Chloroform	Atrazine	PCDD/Fs
	Dichlorobenzenes	Endosulfan	Chlorobenzene
	2,4-dinitrotoluene	Pentachlorobenzene	...
	Methyl bromide	...	
	Isophorone		
	Di- <i>n</i> -butylphthalate		
...			

General Note

Assessment of environmental pollutants is basically based on three principal parameters: the dispersion or accumulation, the (eco)toxic effects and the environmental lifetime or stability.

1.1 Environmental Dispersion and Distribution

Outlook

The dispersion and distribution as one basic parameter for assessing the environmental relevance of organic pollutants are determined by transport and transfer. Fundamental aspects of both processes are discussed in this chapter.

Keywords Transfer • Transport • Partition • Emission pathways • Bioaccumulation • Geoaccumulation

A first main aspect for assessing the impact of organic pollutants on the environment is their distribution and dispersion. Principally two different processes are responsible for the dissemination of organic substances in natural systems: transport and transfer.

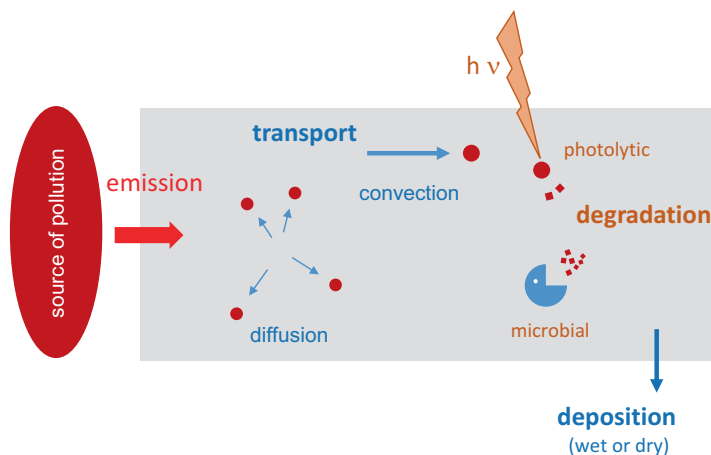


Fig. 1.1 Simple scheme of transportation of pollutants in the atmosphere comprising degradation processes

Transport can be characterized as a movement or spreading within a homogeneous phase. As a first example, pollutants are spread in the atmosphere either as gas or associated with dust. Secondly, dissolved substances or suspensions are moved in river water along the river flow direction. Both processes are clearly triggered by transport processes. Generally, a transport is characterized by a localized emission (the emission source), a movement of the pollutant in the homogeneous phase and finally processes leading to its disappearance. For the movement as well as the disappearance different processes can be responsible. Advection, convection and diffusion are most prominent mechanisms. During the movement, chemical modifications or transformations of the pollutants can occur. Often different processes lead to the same final effect. As an example, diffusion induces a ‘dilution effect’ which can be superimposed by degradation processes also reducing the local concentration of pollutants. Principal schemes of transportation for the atmosphere and the aquifer systems are given in Figs. 1.1 and 1.2.

However, pure transport processes are often important solely for local or even regional distribution phenomena and often on a short time scale. For mid to long term assessment the dispersion of pollutants is more complex. In groundwater systems two transport processes are obvious, a transport as dissolved substances or particle-associated. Further on, during pollutants transport in aquifers a retardation can partly be observed leading to a deceleration (see Fig. 1.2). This is related to adsorption and desorption of substances as interactions located at particle surfaces.

A similar effect can be observed for the atmospheric transport, where consecutive but continuous precipitation and volatilisation slow down the dispersion. For low volatile compounds this transport phenomenon causes a long-scale transport even to very rural or high latitude areas with cold conditions (e.g. arctic regions,

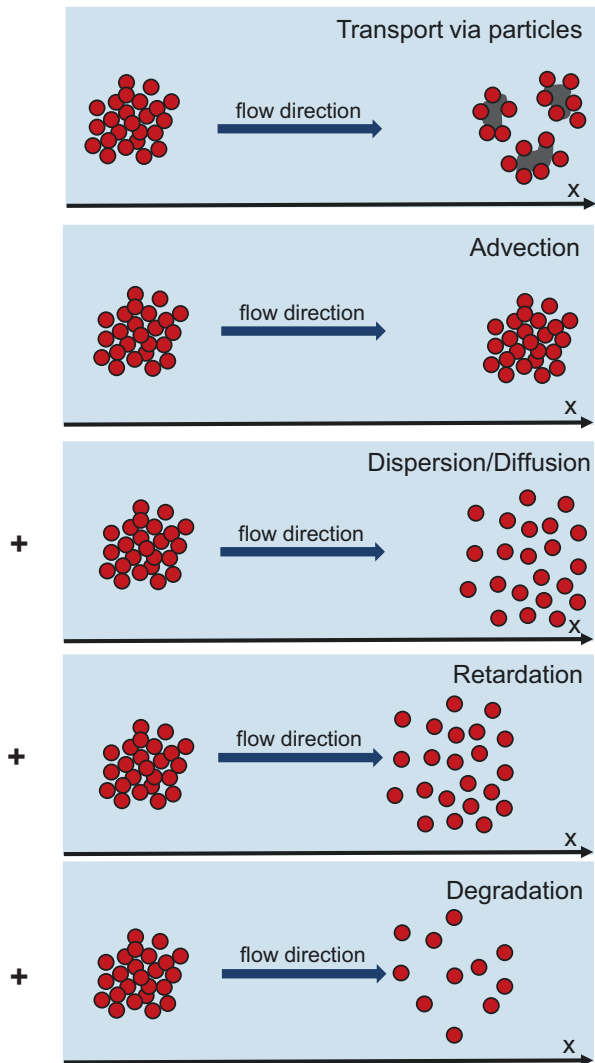


Fig. 1.2 Simple scheme of separate transportation processes in groundwater systems

alpine glaciers) and is often called *Grasshopper Effect* (see Fig.1.3). Low volatile substances remain regionally more restricted.

Higher complexity is valid also for the transport of pollutants in the soil and groundwater systems. Here, horizontal and vertical convection processes as well as retardation, diffusion and density separation can be observed (see Fig. 1.3) that, additionally, differ in the saturated and unsaturated zone.

Principally, transport on a large scale can be observed especially for substances with a high environmental stability or persistence (see Sect. 1.3). For some very

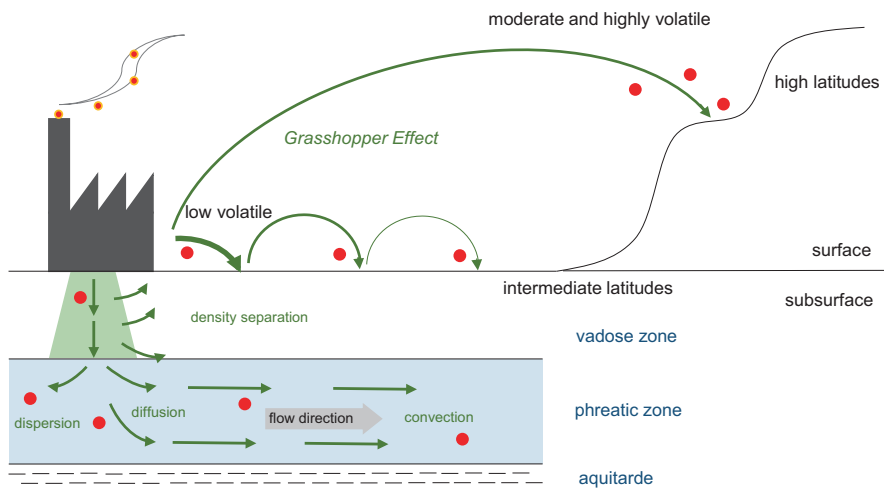


Fig. 1.3 Summary of some principal transport mechanism for pollutants in the atmosphere and the soil/groundwater systems

prominent pollutants (polychlorinated biphenyls PCBs, hexachlorocyclohexanes HCHs and the pesticide DDT) principal higher concentrations have been detected for the northern hemisphere (see Fig. 1.4) as the result of elevated emissions of these compounds in the industrialized countries (most of them situated in the northern hemisphere) and a restricted exchange of air and water between the both hemispheres.

However, for a long-term perspective of disposition and, consequently, the general environmental pathway of pollutants the transfer is more important than the transport. Transfer processes are responsible for the distribution of substances between two different phases. In the environment, the three dominant phases are water, air and particulate matter. This classification corresponds to the three aggregate states, namely solid, liquid and gaseous. These three dominant forms are also represented in global dimensions by the atmosphere, the hydrosphere and the pedosphere. However, also for smaller dimensions the three phases are present. E.g., also the hydrosphere contains gaseous but especially solid matter (sediments, suspended particulate matter SPM). Soil systems consist of the soil particles, the soil air as well as the soil water. A transfer of organic contaminants can be described between small or large-scale phases or compartments. Examples of environmental relevant transfer processes are illustrated in Fig. 1.5.

More generally, the global dispersion can be assumed by transfer processes between the three large compartments pointing to contaminants that are preferably present in the atmosphere, hydrosphere or pedosphere. The same approach is valid for estimating the quantitative distribution of pollutants in smaller ecosystems, such as lakes, forests or coastal regions. A more general scheme of such partitions in the aquatic environment is given in Fig. 1.6.

Global distribution and transport of environmental chemicals

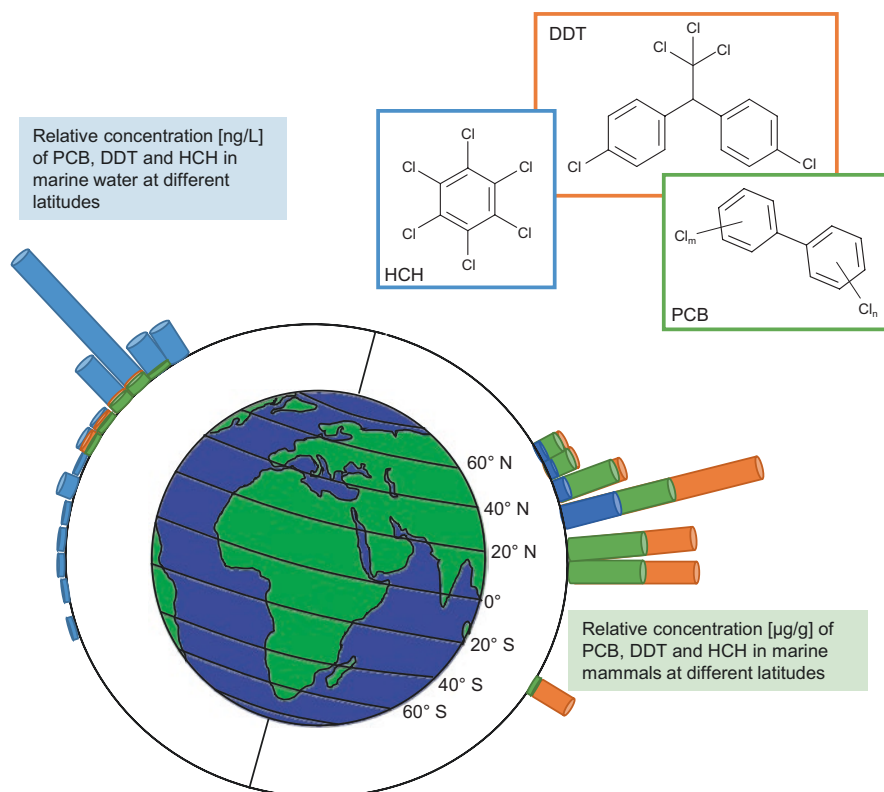


Fig. 1.4 Global distribution of selected environmentally stable pollutants in marine water and mammals (Adapted from and modified after Fent 2013)

But independent from the system scale, the transfer or exchange process of organic substances in environmental systems can be evaluated by a fundamental approach. In steady state conditions, substances are partitioned between two phases as a dynamic equilibrium characterized by constant concentrations in both phases. This partition is described by the law of mass action and the resulting constant value describing this state of equilibrium is the corresponding partition coefficients. Although balanced conditions are normally not gained under natural conditions, the partition coefficients are highly valuable parameters allowing to estimate the accumulation potential for contaminants in the various environmental compartments.

Although interactions between various compartments normally need various partition coefficients, the environmental assessment of chemicals can often be reduced to two most relevant parameters, the Henry Laws constant and the K_{OW} – values.

Fig. 1.5 Typical partition processes in environmental systems

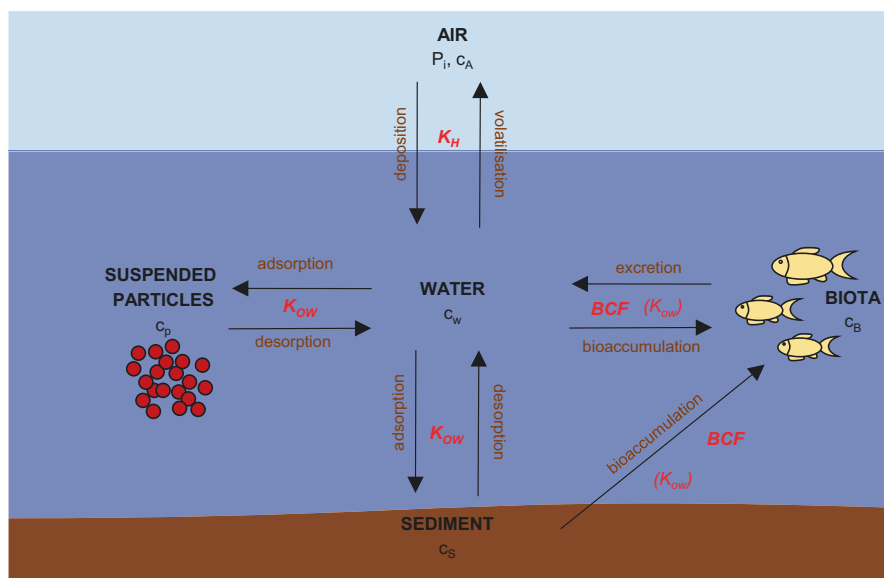
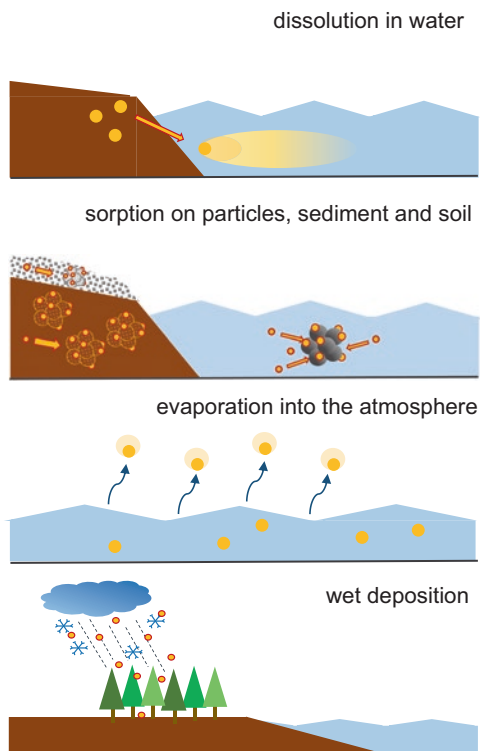


Fig. 1.6 General partition of pollutants in aquatic ecosystems (Modified after Fent 2013)

Henry's law constant

$$K_H = P_i(x) / C_W$$

$$K'_H = C_A / C_W$$

P_i = partial pressure

C_W = concentration in water

C_A = concentration in the gaseous phase

Octanol-water partition coefficient (K_{OW})

$$K_{OW} = C_O / C_W$$

C_O = concentration in 1-octanol phase

C_W = concentration in water

Fig. 1.7 Definitions of two different versions of the Henry Laws constant and the K_{OW} parameter

The Henry Laws constant K_H is given by the ratio of concentration in the gas phase and the liquid phase. Since concentration in gaseous phases can also be expressed by the partial pressure, two different parameters exist as given in Fig. 1.7. Generally, K_H values reflect the tendency of chemicals to accumulate more in the gas phase. High K_H values correlate with lower boiling points and low polarity. K_H values have often high quantities and, therefore, are given normally as $\log K_H$ data. These $\log K_H$ values can be positive but also negative for compounds with low potential to accumulate in the air.

For the partition between particles and water it is difficult to determine a precise value since the solid phase in the environment (soil, sediments, suspended particulate matter, dust etc.) is very heterogeneous. Variations in mineral composition, organic matter quality, particle size and further characteristics do not allow to have one representative solid phase. Interestingly, 1-octanol has been chosen as the phase representing best the partition characteristics of environmental particulate matter, in particular its averaged lipophilicity. Accordingly, the corresponding partition coefficient between water and 1-octanol is called K_{OW} . Its definition is given in Fig. 1.7. Similar to K_H values, often $\log K_{OW}$ values are used. Noteworthy, 1-octanol can be used easily for experimental determination of this partition coefficient since it is a liquid and generates a separate phase in water.

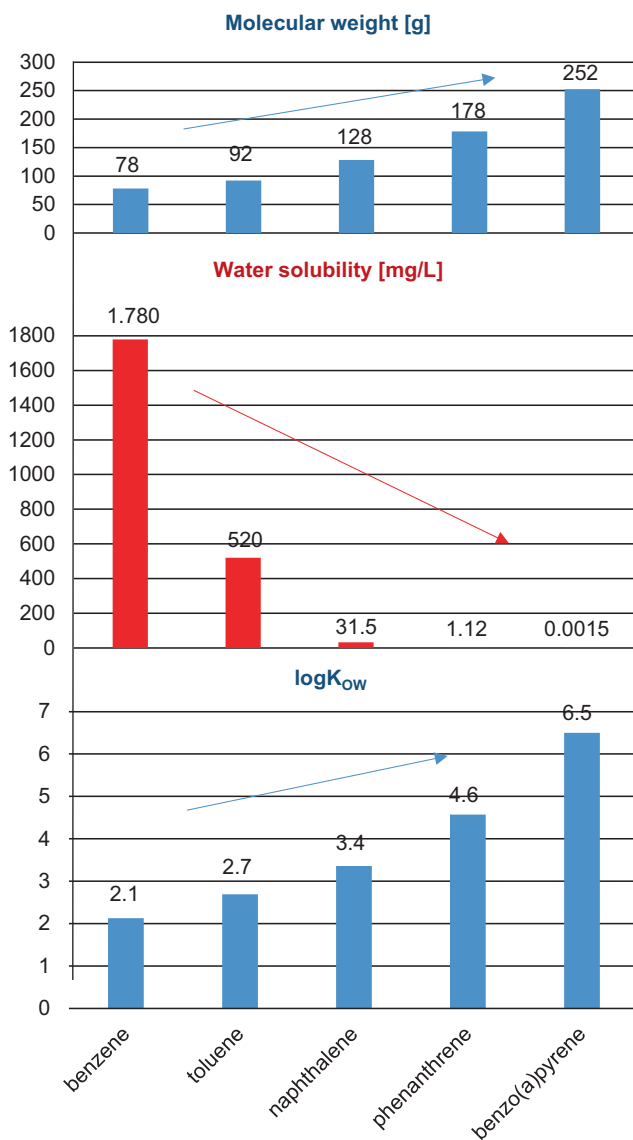


Fig. 1.8 Correlation of logK_{OW} values with molecular weight and water solubility

K_{OW} values are used to generally estimate the tendency of chemicals to adsorb on particles. Higher values are reflecting a higher lipophilicity or a lower hydrophilicity or a lower molecular polarity. Lipophilicity and, correspondingly, the K_{OW} values depend systematically on different molecular properties. For example, lipophilicity and logK_{OW} values increase with increasing molecular weight (see Fig. 1.8) or with increasing degree of chlorination (see Fig. 1.9). On the contrary, polar functional

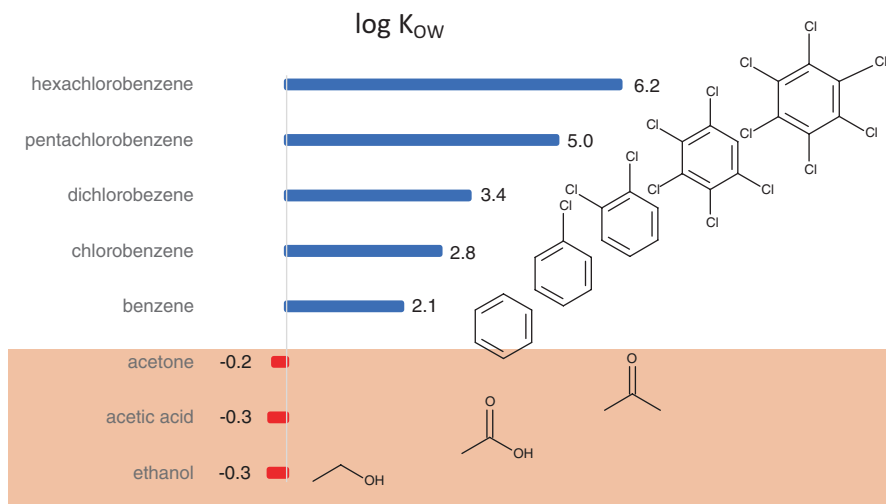


Fig. 1.9 Systematic shift of logK_{OW} values with degree of chlorination for benzenes. Polar functional groups shift the logK_{OW} values towards negative values (Adapted from Bliefert 2002)

groups lower the logK_{OW} values, partly towards negative values (see Fig. 1.9). Opposite trends are visible by comparing molecular structure and water solubility pointing to an obvious direct linkage of partition behaviour and water solubility (see Fig. 1.8).

As already pointed out, two basic physico-chemical properties are most relevant for the principal partition tendency of a pollutant: the polarity and the volatility. Hence, considering these two parameters a rough estimation for the preferred appearance of a contaminant in the three major compartments can be done (as illustrated for some representative organic pollutants in Fig. 1.10). High polarity and lower volatility point to water pollutants, high volatility characterizes air contaminants and a high lipophilicity accompanied with a lower volatility are associated with organic substances appearing dominantly in the particulate matter. In the latter case, a high tendency to occur in particulate matter (soils and sediments) combined with a significant environmental stability leads to the so-called geoaccumulation of pollutants. Geoaccumulation potential is a relevant characteristic for assessing the environmental risk of organic contaminants.

General Note

For environmental risk assessment the long term accumulation of pollutants is the more relevant parameter compared to the short term distribution. This behaviour can be easily estimated by partition coefficients from steady state conditions. Finally, these values depend mainly on two parameters, the volatility and the polarity, that are clearly triggered by the molecular properties. Hence, from chemical structures of pollutants a tendency for environmental accumulation can be directly estimated.

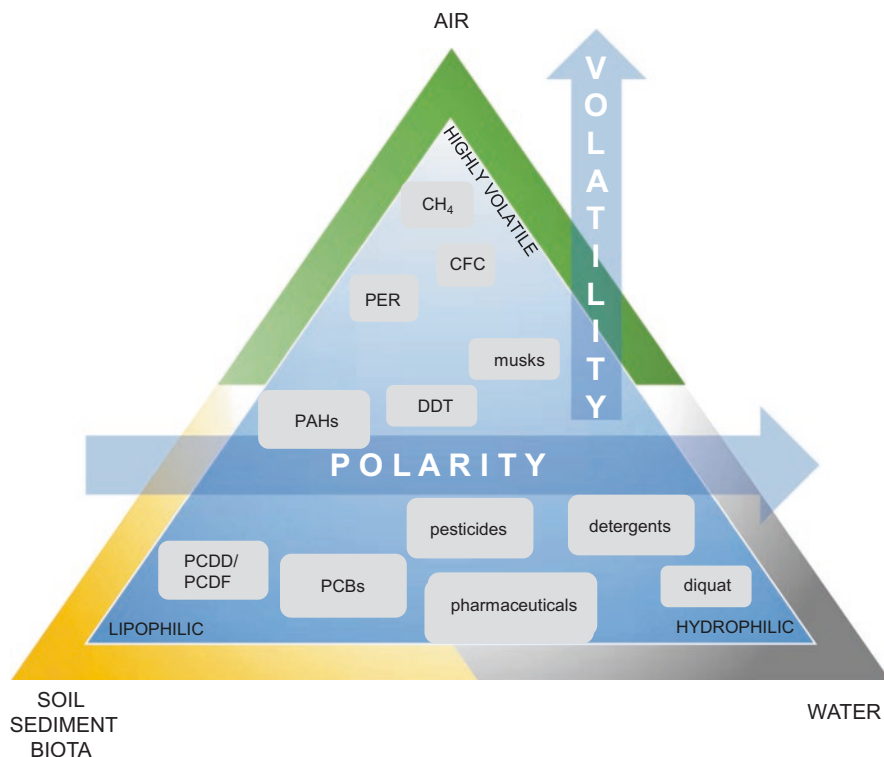


Fig. 1.10 The two major parameters determining the distribution of organic substances, here exemplified for selected pollutants (Modified after Fent 2013)

A preferential accumulation cannot only be roughly estimated. Using the two key parameters for partition, the K_{OW} and K_H values, the distribution behaviour and accumulation potential for chemicals can be assessed quantitatively with a certain precision. Examples for such general dispersion are presented in Fig. 1.11.

One environmental relevant compartment has been neglected so far, the living organisms or so-called biota. For estimating the concentration of pollutants in biota the general approach of equilibrium conditions cannot be applied since the uptake and excretion is not a phase partition.

However, it can be observed in aquatic systems that after a certain time the concentration of organic pollutants in water and biota reach a constant proportion which represents a quasi-steady-state. This process is called bioconcentration and is valid for the direct uptake of pollutants from the surrounding water phase. The corresponding constant ratio is not a partition coefficient but is called bioconcentration factor BCF (see Fig. 1.6) and is also used as a very important parameter for assessing the environmental risk of pollutants. Noteworthy, the BCF depends on the type of pollutant and on the type of organism and differs accordingly for each constellation of species and contaminant. Due to the huge range of values and according to the partition coefficients, also the BCF is often used as $\log BCF$. Interestingly, the

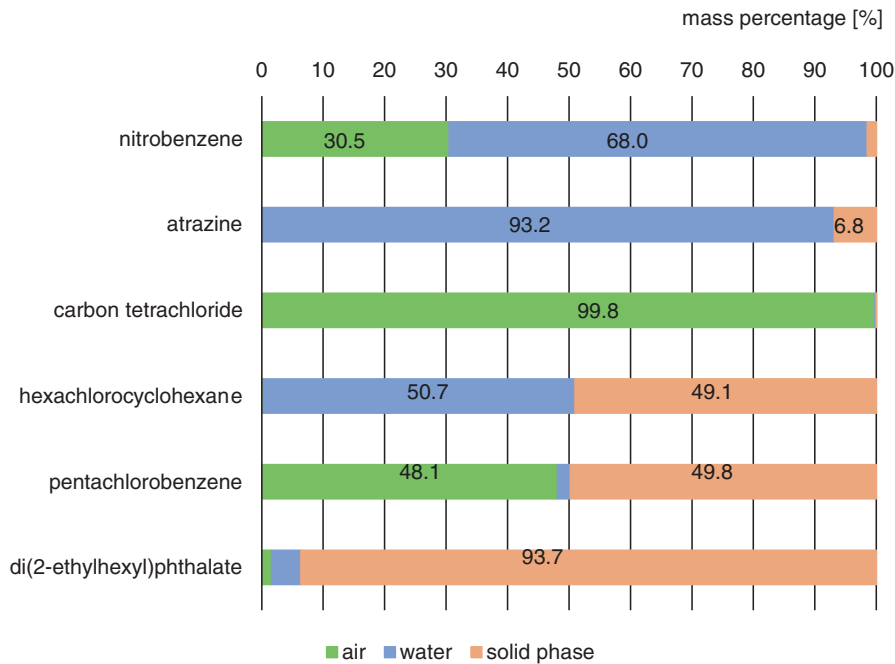


Fig. 1.11 General dispersion of selected organic contaminants based on partition coefficient based calculations (Adapted from Bliefert 2002)

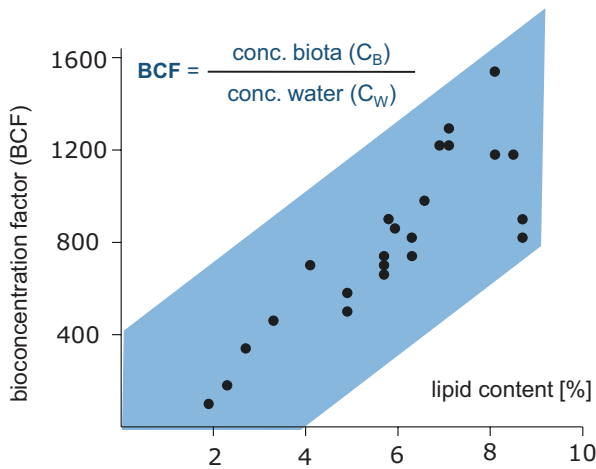


Fig. 1.12 Correlation of BCF and lipid content of organism (Modified after Parlar and Angerhöfer 1995)

BCF increases with lipid content of the organism (see Fig. 1.12). The lipid content is also increasing along the food chain, and, therefore, increasing BCF values with higher trophic levels can be observed (see Table 1.3).

Table 1.3 BCF values along the marine food chain (roughly calculated with data from Bliefert 2002)

Organisms	Calculated level of logBCF _{PCB}
Marine mammals	7.9
Sea birds	7.7
Marine fish	5.7–7.3
Marin invertebrates	6.2–6.7
Plankton	6.6–6.7

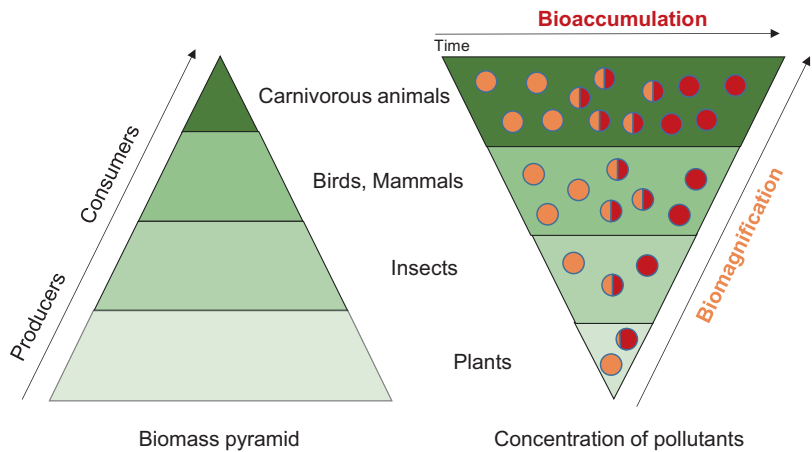


Fig. 1.13 The relationship of trophic levels, contamination levels and bioaccumulation processes

However, this is only one out of two relevant uptake pathways. The second one is the uptake by food. Here a similar process, the biomagnification, can be observed as ratio of concentration level in an organism in relation to the pollution level of the food. This approach implies that biomagnification is often also an enrichment process along the food chain. For this phenomenon, also the increasing lipid content along the food chain is relevant (see Fig. 1.13).

Finally, biomagnification and bioconcentration are both processes that can be summarized as bioaccumulation. And bioaccumulation is one highly relevant property in risk assessments of organic pollutants.

General Note

Biomagnification is relevant as enrichment along the food chain, bioconcentration as enrichment over time till constant levels. Both are the most relevant bioaccumulation processes.

1.2 Toxicological Assessment

Outlook

Toxicological and ecotoxicological effects of pollutants are one major parameter for assessing their impact on the environment. Information on some basic issues are presented in this chapter.

Keywords Ecotoxicity • Acute toxicity • Chronic toxicity • Endocrine disruptors • CMT toxicities

The effect of chemicals on organisms is a very important parameter for evaluating the risk assessment of environmental contaminants but is also a very complex issue. Due to this complexity, only a very brief overview on some basic aspects and principles are discussed here.

In environmental sciences toxicology and ecotoxicology should be differentiated. Briefly, toxicology deals with the impact of chemicals on organisms and ecotoxicology studies the effects of environmental chemicals comprehensively from effects on cells up to an entire ecosystem. Toxicological effects are certainly an important issue in ecotoxicity and both fields have several parts overlapping.

In toxicology some terms used are clearly defined (s. Fig. 1.14) comprising toxicity as an effect and toxicants or toxins as substances responsible for toxicity. Toxins and toxicants just differ by their origin, they represent natural or xenobiotic substances, respectively.

For characterizing toxicological effects three aspects are important: (i) the pathway of exposure, (ii) the frequency and quantity of uptake and (iii) the temporal lag of effect. Poisoning can be overserved principally after two modes of uptake. Firstly, a singular uptake normally with higher doses leading in relative short time periods (minutes to some days) to observable toxic effects represents acute toxicity (see Figs. 1.15 and 1.16). Measurements of acute toxicity in test systems reveal LD_{50} / LC_{50} or EC_{50} values as toxicity parameters (see Fig. 1.16). The parameters represent

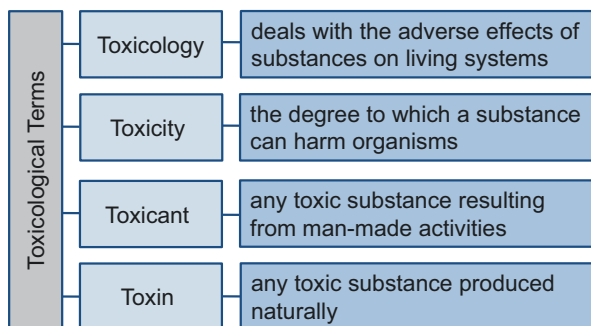


Fig. 1.14 Common terms in toxicology

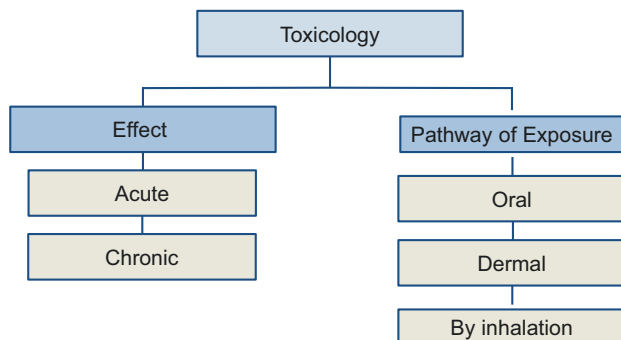


Fig. 1.15 Some basic classifications in toxicology

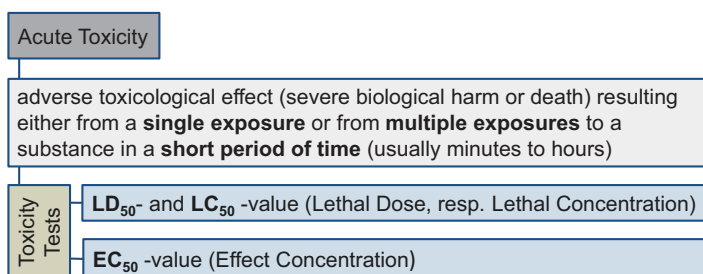


Fig. 1.16 Principles on acute toxicity parameters





either those doses (LD_{50}) or concentrations that causes a lethal (LD_{50}/LC_{50}) or any other toxic effect (EC_{50}) for 50% of observed test organisms in a defined but relatively short time period and after a single dose or short time of application.

Acute toxicity is an important parameter for assessing the risk of chemicals. Accordingly, it is used frequently in various systems for categorizing and evaluating the toxic potential of substances. One example is related to the Globally Harmonized System (GHS) developed by the UN for classification and labelling of chemicals (see Fig. 1.17).

A more simple system categorizing toxicants and toxins based on acute toxic effects is given in Fig. 1.18. Here, the ingested doses are used for a rough classification of toxic compounds.

A second type of toxicity is characterized by a continuous exposure for a longer time period, where the toxic effects are observed after a certain time lag. The applied doses or concentrations of uptake are commonly much lower as compared to acute toxic doses. As an important aspect of chronic toxicity, the toxic effects appear after a longer time period, from month to even decades. Here, a clear linkage of toxicant or toxin to the toxic impact is often difficult to diagnose. Tests for chronic toxicity provide two types of parameters which are very similar in terms of absolute values. These are threshold values that are converging from two opposite directions (see Fig. 1.19 and 1.21). The NOEL or NOEC values start from doses or concentrations which do not cause toxic effects and the threshold is the highest value that is conform

Acute Toxicity according to Globally Harmonized System (GHS)

Acute Toxicity	Category 1	Category 2	Category 3	Category 4
				
	Toxic	Toxic	Toxic	Harmful
Oral (mg/kg)	< 5	5 - 50	50 - 300	300 - 2000
Dermal (mg/kg)	< 50	50 - 200	200 - 1000	1000 - 2000
Gases (ppmV)	< 100	100 - 500	500 - 2500	2500-20000
Vapours (mg/l)	< 0,5	0,5 - 2,0	2,0 - 10,0	10,0 - 20,0
Dusts / Mists (mg/l)	< 0,05	0,05 - 0,5	0,5 - 1	1 - 5

Quelle: Verordnung (EG) Nr. 1272/2008, S. 81

Fig. 1.17 Acute toxicity as one index for categorization within the Globally Harmonized System (GHS)

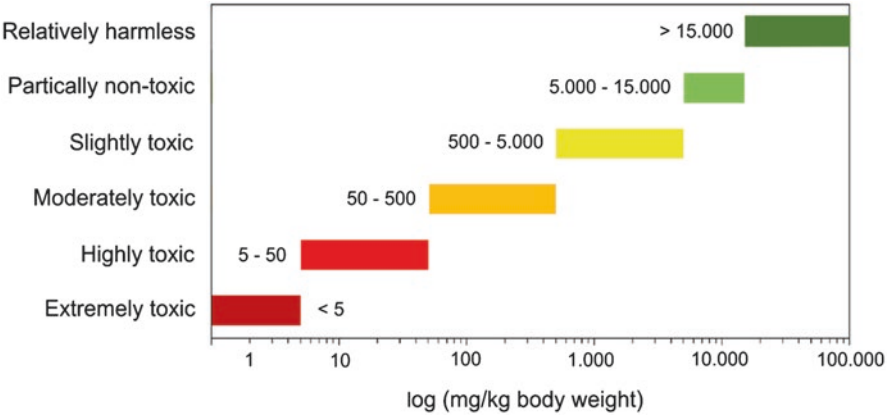


Fig. 1.18 Classification of toxicants based on the lethal dose for humans (Adapted from and modified after Rodricks 1992)

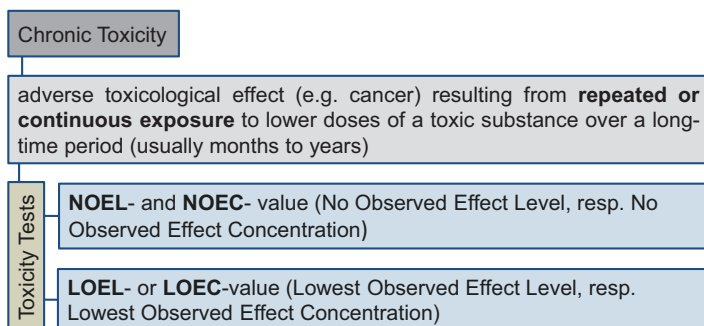


Fig. 1.19 Principles and definitions of chronic toxicity parameters

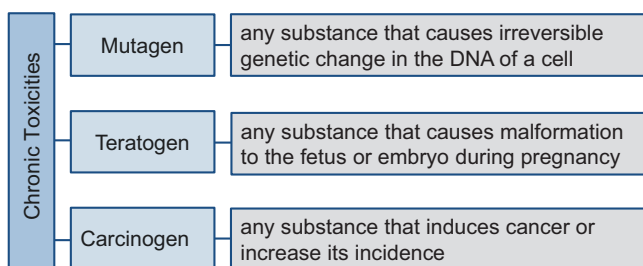


Fig. 1.20 The so-called CMT toxicities

with this characteristic (highest level/concentration with no observed effect). On the contrary, LOEL or LOEC represents an approximation from observed toxic effects, where the concentrations are decreased towards the lowest value for which an effect is observed.

Most relevant chronic toxicities considered in many risk assessments for chemicals are carcinogenicity, mutagenicity and teratogenicity also abbreviated as CMT (see Fig. 1.20). The corresponding effects can be attributed to genotoxic effects harming the DNA and the corresponding processes of replication, transcription etc.

Ecotoxic effects often do not appear in a linear correlation between concentration or dose and observed intensity of the toxic effect. The relation is mainly characterized by a period where no effects are observed followed by an exponentially increasing effect that reaches a saturation level (see Fig. 1.21). The relative small concentration range between rise and stagnation characterises the transition from non-toxic to toxic conditions. For assessing the NOEL(C) or LOEL(C) values a threshold (e.g. 20%) is defined as the beginning of the effect.

Such dose-response relationships are measured and used in ecotoxicological test systems. These tests are created with different test organisms, measured effects and time periods. All parameters are optimized with respect to the environmental compartment (hydro- or pedosphere), to the biological species (mammals, invertebrates etc.) and to the type of toxicity (acute or chronic). A selection of ecotoxicological tests and their parameters are summarized in Table 1.4.

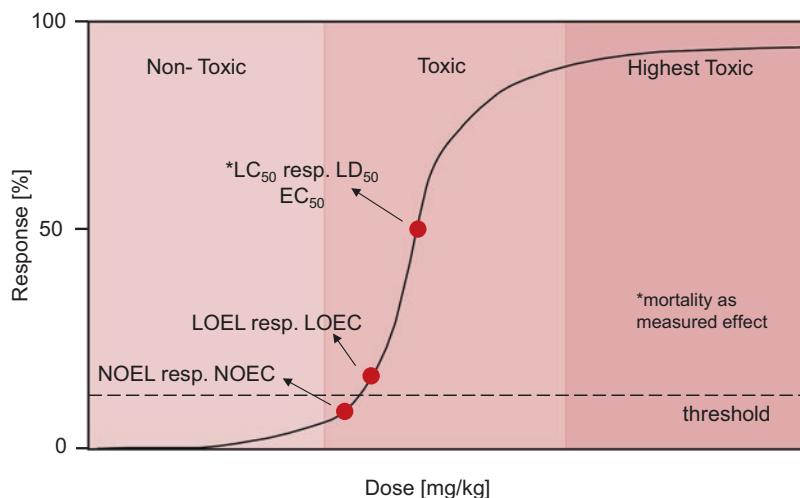


Fig. 1.21 Scheme of a usual dose-response relationship measured in ecotoxicological tests (Modified after Fent 2013)

Table 1.4 Common ecotoxicological tests and key parameters

Organism	Effect	Time/ Toxicity parameter
Acute toxicity		
Bacteria	Luminescent bacteria test, metabolic activity	15–60 min, EC_{50}
Alga	Growth inhibition test	72 h, EC_{50}
Daphnia	Immobilisation, mortality	24 h, LC_{50}
Fish	Acute Toxicity, mortality	96 h, LC_{50}
Chronic toxicity		
Bacteria	Growth inhibition test	Hours, NOEC
Alga	Growth inhibition test, chlorophyll fluorescence	72 h, NOEC
Daphnia	Reproduction	21 d, NOEC
Fish	Extended fish test, mortality, symptomology	14 d, 21 d, NOEC

Several specific aspects have to be considered by assessing the toxicity of chemicals, e.g. molecular structures comprising the stereochemical properties, effects of metabolites, sensitivity for different species and for different biological points of attack as well as at different growth stages.

One well known example for stereochemical properties and their implications for toxicity is the pharmaceutical Contergan® whose main active ingredient is thalidomide. Thalidomide exhibit one chiral carbon atom and, correspondingly, both enantiomers, the R- and the S- form, exist (see Fig. 1.22). The stereoisomers exhibit different effects on humans, the R-isomer is a sedative as desired, but the S-enantiomer exhibits teratogenic properties. This effect led to the so-called Contergan Catastrophe in the beginning 1960s. Taking this pharmaceuticals during

Excursus – Acute vs chronic toxicity

Assessing an environmental substance both toxicities have to be considered and compared. Often the differences between the corresponding parameters (concentrations) are high leading to the importance of only one toxicity, normally the chronic toxicity. If chronic toxicities (NOEC values) are much lower than acute toxicity parameters (LC_{50} etc.), these toxicological effects are more important and, consequently, need primary attention. If acute and chronic toxicities are measured on similar concentration levels the acute toxicity becomes more important and is more relevant than the chronic one. These constellations are exemplified in the following table.

Table: Acute and toxic toxicity parameters measured for different pesticides and fish species. Constellations, in which chronic toxicity is highly relevant, are marked in blue, whereas those combinations are highlighted in red that needs more attention on the acute toxicity (Simplified and modified after Fent 2013)

Pesticide	Fish species	Effect	LC_{50}	NOEC	$LC_{50}/NOEC$
Carbaryl	Pimephales promelas	Survival $F1^2$	9.0	0.021	428
Chlordane	Lepomis macrochirus	Number of eggs	0.06	0.005	11
Endrin	Jordanella floridae	Number of eggs	0.0009	0.0002	4
Kepone	Cyprinodon variegatus	Growth	0.3	0.0001	2833
Malathion	Jordanella floridae	Growth	0.3	0.014	23
Parathion	Lepomis macrochirus	Deformation	0.5	0.0003	1500

pregnancy induced serious defects on unborn children. Unfortunately, both enantiomers are interconvertible via a simple intramolecular rearrangement as depicted in Fig. 1.22. Consequently, the teratogenic effect cannot be eliminated e.g. by isolating only the R-isomer. Nowadays, Contergan® is used very limited against leprosy and specific forms of cancer under very strict control.

As a second aspect, the magnitude of toxic effects depends not only on the chemicals but also on the target species. This can be illustrated by acute as well as chronic toxicities tested on different species and the variation of the corresponding toxicity values as illustrated in Fig. 1.23. No clear preference is visible and, consequently, the extent of toxic effects on different organisms do not seem to be predictable systematically.

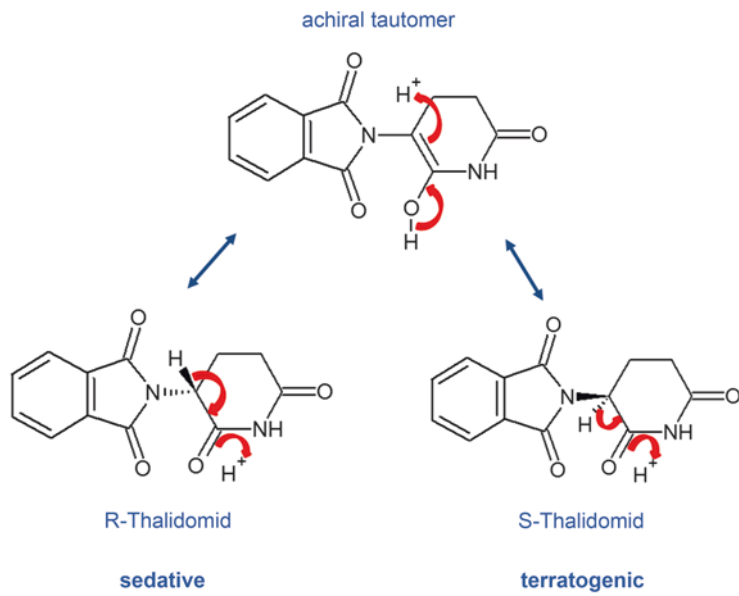


Fig. 1.22 Enantiomers of thalidomide and the pathway of interconversion

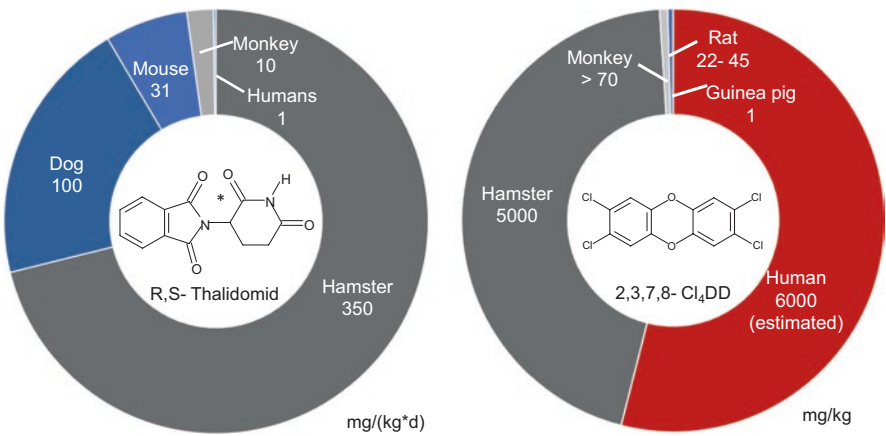


Fig. 1.23 Variation of lethal doses (right side) or lowest effective daily doses (left side) for two chemicals thalidomide and 2,3,7,8-tetrachlorodibenzodioxine, also called Seveso dioxin (see Sect 2.1.), with respect to different target species (Data taken from Bliefert 2002; Alloway and Ayres 1996)

Table 1.5 Various toxic effects on different biological levels (Simplified after Fent 2013)

Category	Environmental chemicals
Low-specific parameters	
Reduction of growth	Several Triphenyltin
Delayed metamorphose (frog)	Thiocyanate, Nonylphenol, DDT
Impairment of reproduction	
Reduction of the egg cell/ sperm	Thiocyanate
Thinning of eggshells (birds)	DDT, Dieldrin
Change of physiological functions	
Blood parameters	Pesticide
Respiration	Cyanide
Behavioural change	
Reduced enemy avoidance	Narcotic substances
Increased disease incidence and parasites	
Immunotoxicity	Organotin compounds
Indirect effects	
Loss of nutrients, nutrient plants	Pesticide
Loss of predators (zooplankton)	Organophosphate insecticides

Beside toxic symptoms that can directly be measured or are quite clear and obvious, further effects can be attributed to chemicals with a more non-specific or disguised appearance. Hereby influences on organism can occur on different biological and ecosystematic levels. Impacts on a cell scale are often well identifiable but harmful long-term changes on ecosystems are less evident. This comprises e.g. loss of predators, delayed metamorphoses, decrease of population. A linkage of types of pollutants and different symptoms of chronic toxicities on various ecosystem levels are summarized in Table 1.5.

Toxic impacts on organisms can also be differentiated at different stages of life-cycles and for different chemicals. It is important to note, that defined toxicants can take effect at certain steps of lifecycle as exemplified for some common pollutants in Fig. 1.24. This knowledge is important to evaluate the specificity of toxications by different substances and their implications for the impact on ecosystems.

As a further aspect of a more comprehensive view on toxic potentials of environmental chemicals, the properties of metabolites or transformation products should be considered. A very well studied example on how the toxic risk can change with metabolism is related to PER, the perchlorinated ethane (detailed information on this pollutant is given in Sect. 2.1). Dehalogenation forms different metabolites with decreasing number of chlorine atoms but with changing acute and chronic toxicity as summarized in Fig. 1.25. In comparison to the precursor a first increase in acute but also an occurrence of mutagenicity and probably carcinogenicity is observed as long as the metabolites possess chlorine moieties. Finally, just after the release of the last chlorine atom from vinylchloride the toxicity decreased substantially.

A special type of chronic toxicity got a higher attention in the last two decades, although the corresponding effect is known since the 1950s (see Fig. 1.26). Toxicants

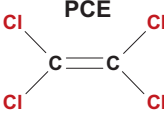
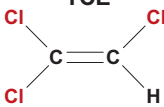
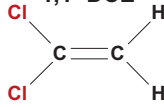
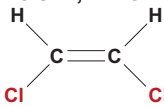
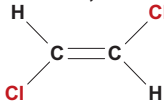
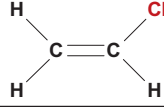
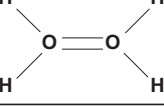
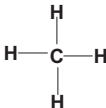
Compound	Mutagenicity (Ames-Test)	Carcinogenicity (animals tested)	LD ₅₀ (g/kg)	
			rat	mouse
<div>PCE </div>	+	-	2.6	8.8
<div>TCE </div>	+	S	4.9	2.4
<div>1,1- DCE </div>	+	S	0.2	
<div>cis- 1,2- DCE </div>		-	0.8	
<div>trans- 1,2- DCE </div>		-	0.5	
<div>VCM </div>	+	+		
<div>Ethene </div>				
<div>Methane </div>				

Fig. 1.24 Exemplified impact of selected pollutants at different stage of lifecycles of organism (Simplified after Vasseur and Cossu-Leguille 2006)

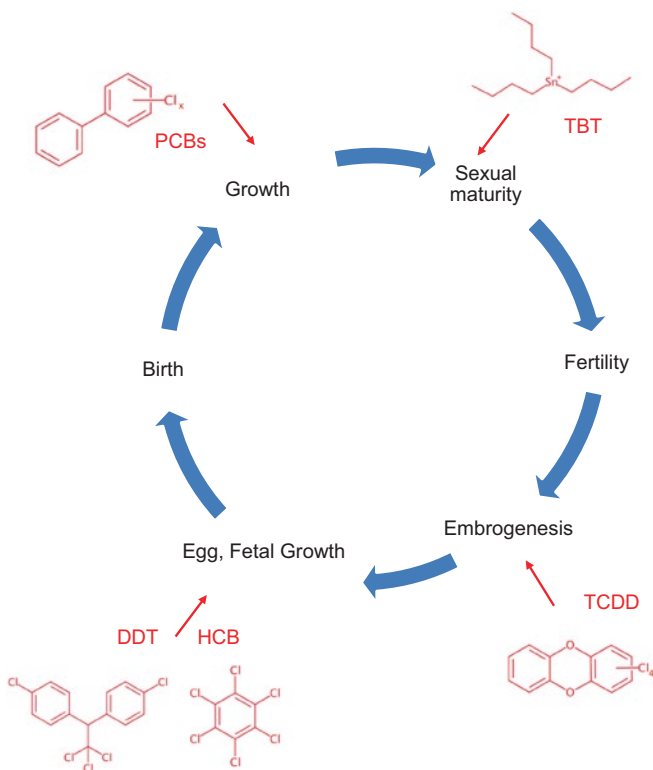


Fig. 1.25 Development of acute and chronic toxicity along a main degradation pathway of tetra-chloroethene PER (+ = positive result; - = negative result; S = suspected) (Adapted from and modified after Fent 2013)

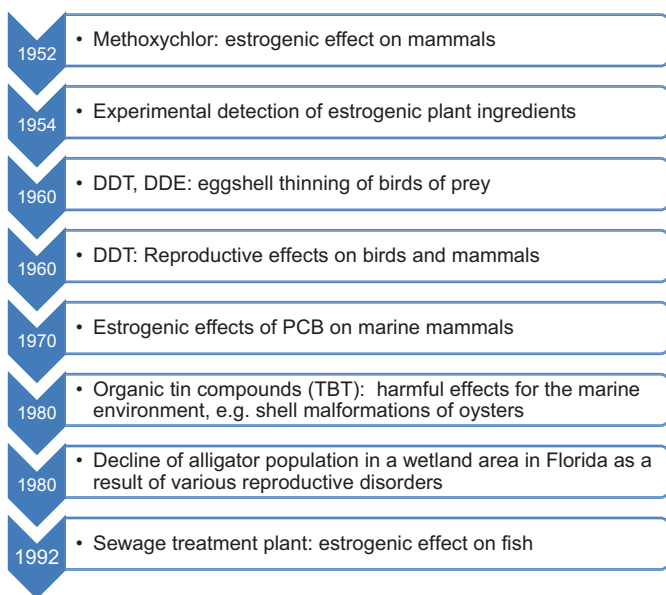


Fig. 1.26 Historical awareness of endocrine disrupting chemicals (Adapted from and modified after Fent 2013)

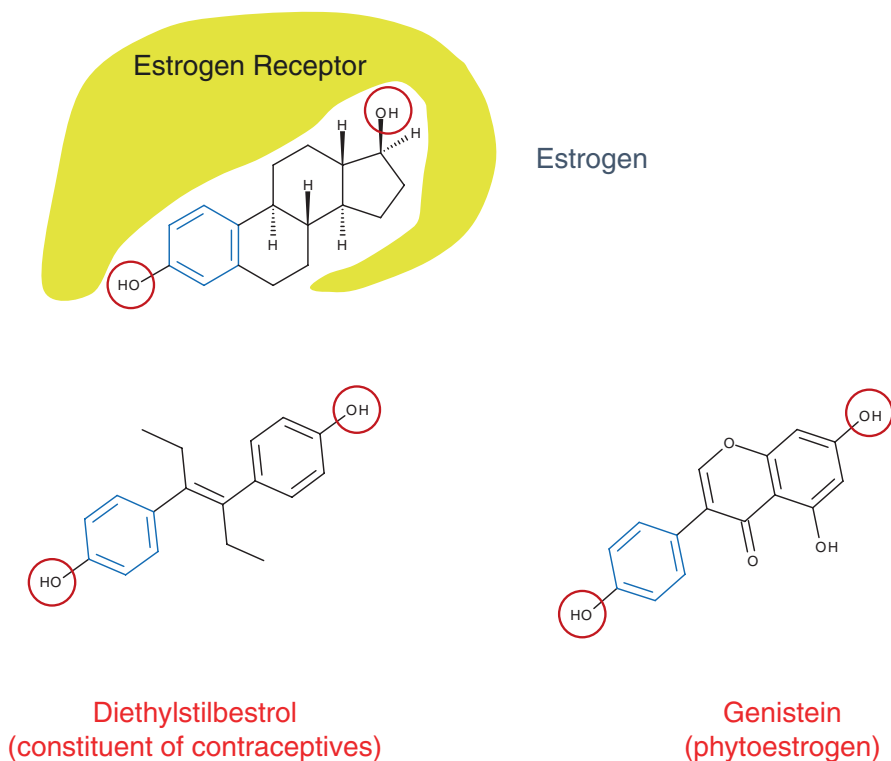


Fig. 1.27 General approach on how endocrine disrupting compounds interact with receptors

that act in organisms in a way similar to hormones are called endocrine disruptors. These substances disrupt the endocrine systems leading to a variety of different symptoms. This phenomena is based on the chemical and structural similarity of endocrine disruptors with natural hormones. As a result of these similarities the endocrine disruptors can enter receptors of the endocrine systems (e.g., the estrogen receptor as illustrated in Fig. 1.27) inducing unintentional biochemical and physiological reactions. Well known impacts are changes in blood levels of hormones, alteration of sexual organs, influences on sperm production rates or egg growth and many more abnormal effects.

Noteworthy, some substances with hormone-like properties are of natural origin appearing for example in plants (e.g. genistein or β -sitosterol), also named phytoestrogens. However, much concern is related to the xenobiotic endocrine disruptors with a wide range of applications. Well known are bisphenol A as widespread used technical agent, some pesticides including DDT metabolites, synthetic steroids and

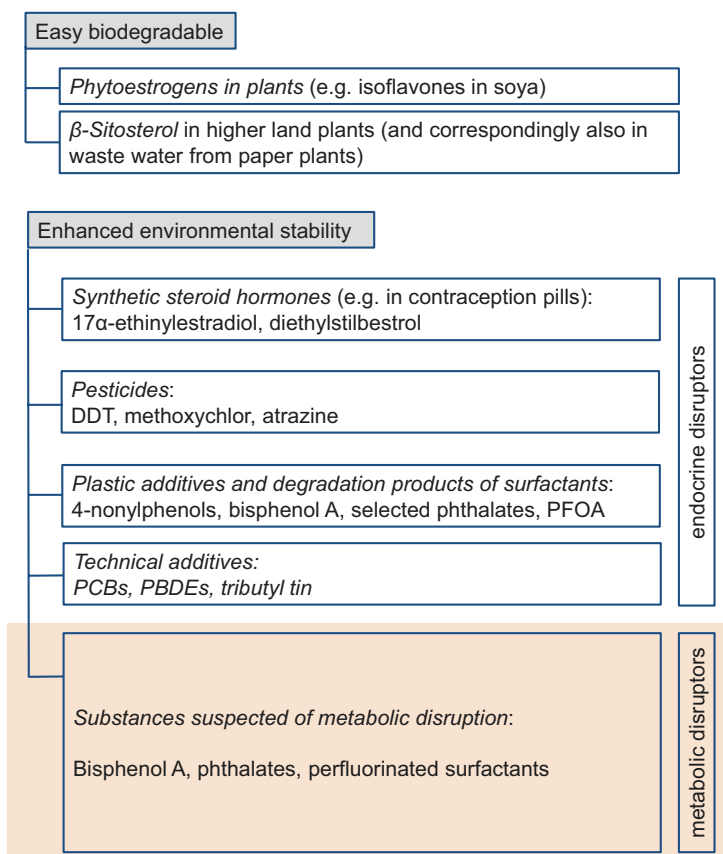


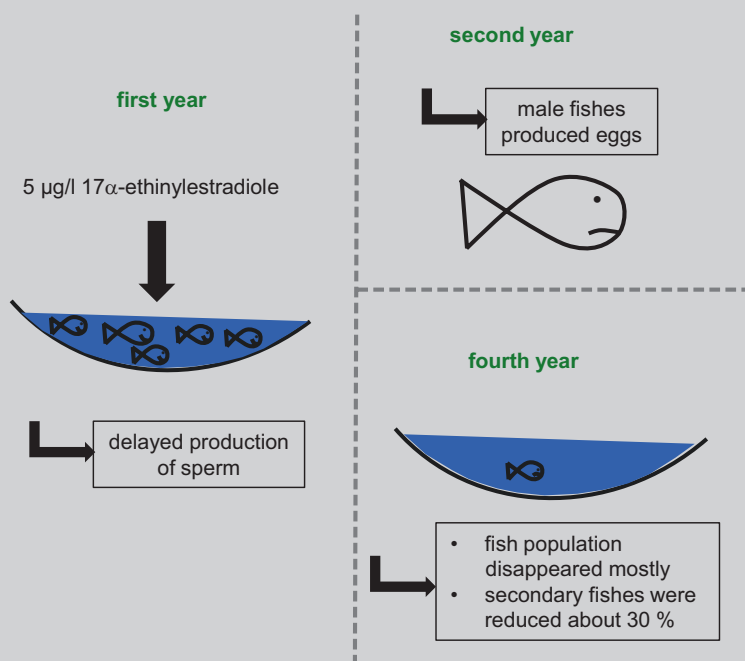
Fig. 1.28 Endocrine disruptors and substances with corresponding effects on metabolism (adapted and expanded from Fent 2013 and Heindel et al. 2015)

plasticizers like phthalates (see Fig. 1.28). Since these effects are a kind of chronic toxicity, a longer exposition with lower doses or concentrations is needed to induce the harmful effects.

Recently also environmental chemicals influencing further systems in organisms receive upcoming attention. As one example, the influence of compounds, foreign for human bodies, on the metabolism cycles are currently under investigation (see Fig. 1.28). Interestingly, suspected chemicals comprises also bisphenol A or phthalates.

Excursion – How fast and with which sensitivity reacts an aquatic ecosystem to contamination by endocrine disruptors?

A case study revealed interesting insights into the sensitivity of aquatic ecosystems regarding pollutions by endocrine disruptors (Kidd et al. 2007). During the 5-year experiment the effects from a permanent contamination of a fish population by an endocrine disruptor (17 α -ethinylestradiol) was followed. The estrogenic effects became rapidly evident within the first years, finally by a substantial decrease of population including secondary fish species. This experiment pointed to a very rapid response of an aquatic species to endocrine disrupting contamination including its implications for the corresponding ecosystem.



Noteworthy, this experiment certainly does not provide general information on the ecosystems' sensitivity but points to the potential of relatively fast responses also to low doses of emissions.

General Note

Toxic and ecotoxic effects of chemicals are very complex and depend not only on the chemical and structural properties of the toxicants but also on the target organism and their biological target points.

1.3 Transformation and Degradation

Outlook

Transformation or even degradation of organic contaminants is a further key parameter for risk assessments of organic pollutants. Principal aspects of transformation are described distinguishing abiotic and biotic processes as well as aerobic and anaerobic conditions.

Keywords Abiotic degradation • Biotic degradation • Metabolism • Degradation pathways • Persistence • Aerobic degradation • Anaerobic degradation

The second important parameter for evaluating the environmental risk of organic contaminants is their chemical transformation and degradation potential. As a primary aspect, the environmental stability or persistence has to be considered. Persistence in a very strict manner (no chemical transformation in any time period) cannot be attributed to organic pollutants, since every organic substance underlies degradation someday. However, in organic environmental geochemistry a prolonged environmental stability e.g. expressed by long environmental half-life times has accounted as persistence. These persistent pollutants exist unaltered in time periods ranging from several months to years depending on the compartment (see Table 1.1 as example for evaluating persistence based on extended half-life times).

A basic classification of transformation processes is based on the involvement of organisms. Beside abiotic transformations, the biotic conversions and degradation have to be considered. Abiotic degradation plays an important role in the atmosphere and the top layers of aquatic and soil systems. Dominant trigger for chemical transformations is radiation and the resulting photolysis and activation of chemical species. Here, oxygen species are responsible indirectly for many abiotic reactions. As an example, photolytic induced oxidation has been observed for polycyclic aromatic hydrocarbons PAH (see Sect. 2.7) in the photic zone of surface water systems as well as in the atmosphere (see Fig. 1.29). The initial reaction is the photo activation of oxygen followed by its addition to an aromatic system forming an oxygen-containing ring system. This system is further oxidised to quinone moieties.

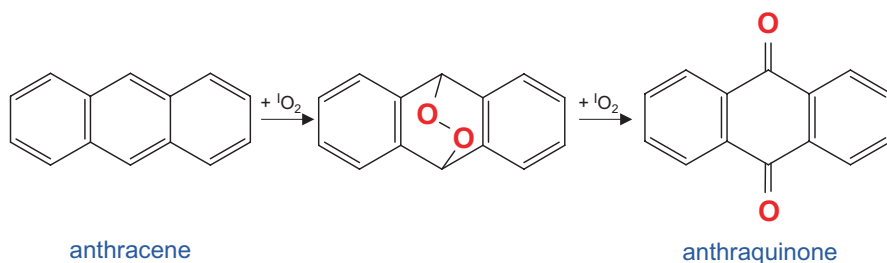


Fig. 1.29 Abiotic oxidation of anthracene by activated oxygen (After Parlar and Angerhöfer 1995)

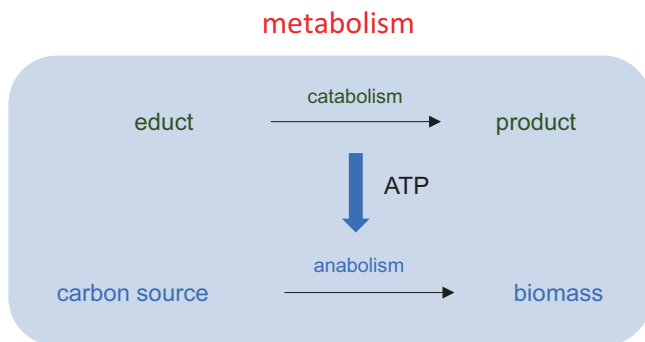


Fig. 1.30 Schematic differentiation of the two major metabolism pathways (Modified after Reineke and Schlömann 2007)

From a more chemical point of view, the main abiotic transformation can be attributed to oxidations and hydrolysis. The latter reaction cleaves hydrolysable linkages such as esters or amides. To a very minor extent also abiotic reduction has been observed under anaerobic conditions e.g. in sediments.

Generally, biotic transformation has a much higher importance for the environmental fate of organic pollutants as compared to abiotic processes. As described in detail for natural products in the second volume of this book series ('From biomolecules to chemofossils', 2nd Vol of *Fundamentals of Organic Geochemistry*, Sect. 1.3) especially microorganisms are responsible for a dominant metabolic rate.

In principal, the biotic conversion or metabolism of organic substances can be divided into two different pathways, a first transformation of educts with the aim to obtain energy (in the form of biochemically stored energy by ATP formation), the so-called catabolism, and a second pathway synthesizing the biomass of an organism, the so-called anabolism (see Fig. 1.30).

An environmentally important problem is the transformation of xenobiotic compounds. For organic xenobiotics a general metabolism pathway can be described for higher organisms with three different phases (see Fig. 1.31). A first phase converts or transforms the pollutants e.g. by hydrolysis, oxidation or reduction to phase I metabolites. Aims of such transformations are e.g. to enhance the water solubility, to insert functional groups for further reactions (phase II reactions) or to detoxify. If these metabolites cannot be subjected to the anabolic or catabolic metabolism, organisms try to get rid of these substances in a second phase, in which they are linked to conjugates like glutathione, amino acids, or glucuronic acid for subsequent excretion or incorporation (phase III).

As an important aspect, all biotic transformations, in particular phase I and II reactions, are enzyme initiated and assisted. Main types of phase I reactions are oxidation, reduction and hydrolysis initiated e.g. by esterase, reductase or cytochrome P450 oxygenase. These enzyme systems are dominantly located in the cytosol or the endoplasmic reticulum. Hence, water solubility is an important property enhancing the interaction with enzymes and consequently, fasten the transformation

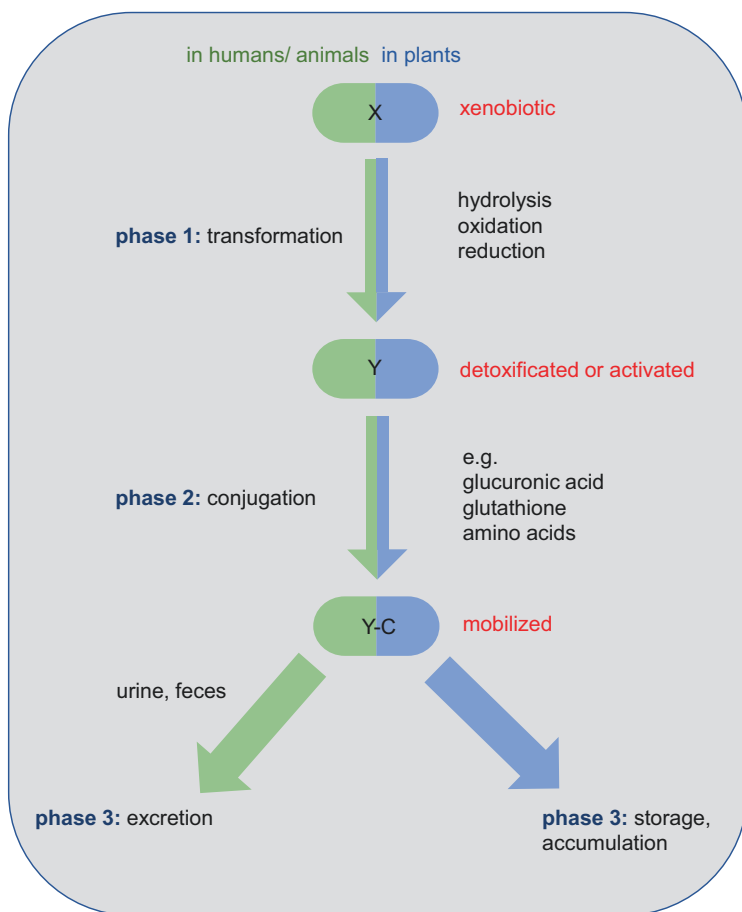


Fig. 1.31 Principle scheme of pollutant conversion and excretion in higher organisms

rate. Additionally, it is an important precondition for transformation that the organic substances fit into the active slot of the responsible enzymes. If this precondition is not fulfilled, a transformation and subsequent degradation or excretion is hindered. This accounts in particular for steric hindrances, e.g. due to branched carbon chains, and explains why some xenobiotics are less biodegradable (e.g. tetrapropylene based alkylbenzene sulfonates ABS as compared to linear alkylbenzene sulfonates LAS, see Sect. 2.4).

Xenobiotics do not exist naturally but have been synthesized exclusively by humans. Therefore, biological tools to convert these substances (as described above) are often not optimized or work in an inefficient way. One alternative possibility for a degradation of xenobiotics is the principle of cometabolism. If xenobiotics exhibit a higher structural similarity to natural products they can be converted in parallel as

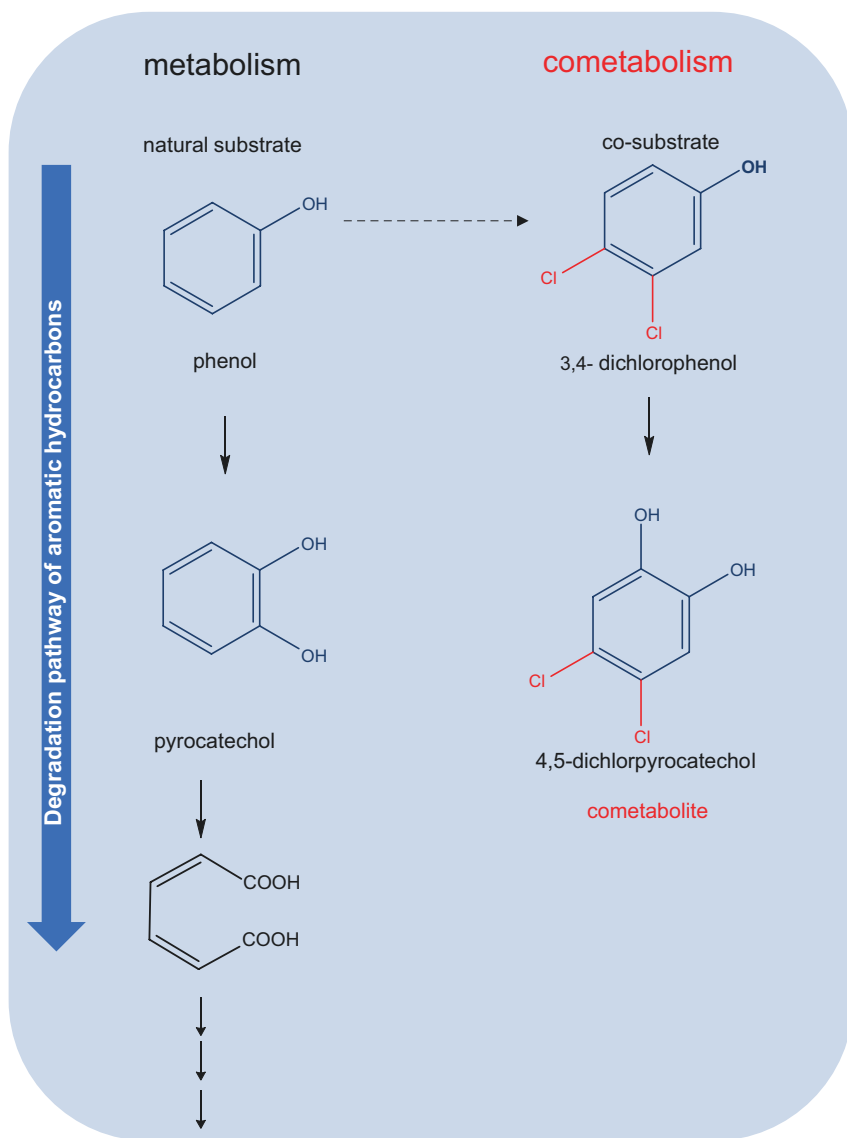


Fig. 1.32 Cometabolisms of chlorinated phenols (Simplified after Reinecke and Schlömann 2007; Fritsche 1998)

illustrated in Fig. 1.32. However, these conversions are usually induced by less specific reaction pathways and do not provide remarkable energy for the organism, since the cometabolic reactions normally do not lead to an extended degradation or even mineralisation.

In environmental systems, the highest contribution to pollutant removal by degradation is related to microorganisms. Here, aerobic and anaerobic conditions and the corresponding microbial communities have to be differentiated. Very roughly, under aerobic conditions faster degradation rates can be stated leading often to a complete degradation (mineralisation). Conversion rates in anaerobic compartments are generally lower and, correspondingly, half-life times are prolonged and often incomplete.

In the following, some main transformation pathways of pollutant classes or structural moieties under anaerobic and aerobic conditions are briefly introduced. Numerous conversions can take place if already functional groups exist. Hydrolysable groups e.g. in phosphate based pesticides or phthalate based plasticisers can easily be cleaved by hydrolysis as an initial metabolism step which is exemplified in Fig. 1.32. Functional groups sensitive for oxidation or reduction are convertible preferentially under aerobic or anaerobic conditions, respectively. As an example, nitro groups can be easily reduced under anaerobic conditions to amino groups, an important transformation for explosives (see Sect. 2.6). Organic sulphides exhibit the potential to be oxidized which has been reported e.g. for methylthiolated PCBs. These first metabolites are subsequently oxidized to sulfones under aerobic conditions (see Sect. 2.1). Noteworthy, also combined oxidation and reduction can be observed e.g. by exchange of functional groups. This is illustrated in Fig. 1.33 for the substitution of nitro by hydroxy groups in an aromatic substance.

From an environmental point of view, special attention has to be given to halogenated, in particular chlorinated, pollutants and their degradation or transformation, because they often exhibit a high persistence. Dehalogenation occurs under aerobic and anaerobic conditions at both aliphatic and aromatic backbones.

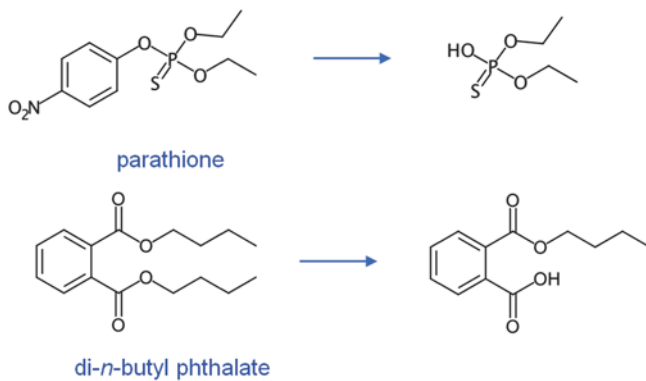
A common pathway is the hydrolytic cleavage of C-Cl bonds replacing chloro substituents by hydroxy groups. In parallel, the substitution of chlorine by thio ethers is a thiolysis. Under aerobic conditions also oxidizing mechanisms allow to substitute chlorine dominantly by oxygen containing groups. On the contrary, a direct exchange of chlorine by hydrogen is an anaerobic mechanism and often observed in aquatic sediments. A systematic and exemplifying overview on these common dechlorination mechanisms for aliphatic and aromatic pollutants is given in Fig. 1.34.

Noteworthy, these dehalogenation mechanisms do not necessarily appear isolated. For numerous substances dehalogenation pathways are known, in which different mechanisms are used subsequently. An example is presented in Fig. 1.35.

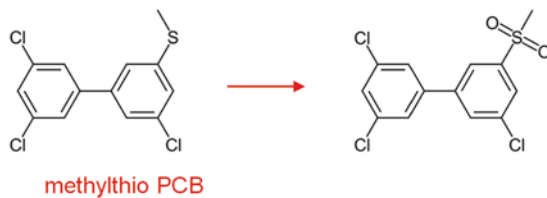
Transformation and degradation certainly appears not only at functional groups but also aliphatic and aromatic hydrocarbon moieties are subject to conversion. Due to their different chemical properties, aliphatic moieties underlie different transformation reaction compared to aromatic compounds. For both a much higher transformation rate under aerobic conditions as compared to anaerobic environments are evident.

Aliphatic carbon chains can be shortened under aerobic conditions by oxidation forming carboxylic acids and subsequently by a so-called β -oxidation, the biochemical cycle to cleave acetic acid moieties (as acetyl coenzyme A, AcetylCoA) by oxidation. The result of such reaction cycle is a new carboxylic acid shortened by 2

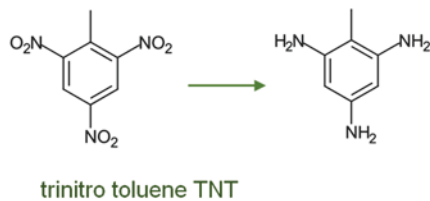
hydrolysis



oxidation



reduction



oxidation + reduction

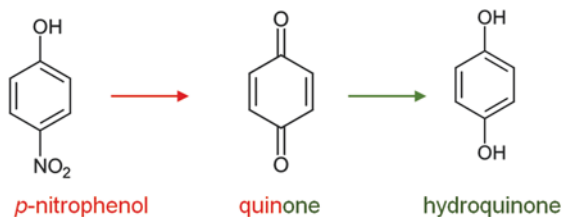


Fig. 1.33 Some exemplifying microbial conversions of functional groups in organic pollutants (Simplified after Reinecke and Schlömann 2007; Parlar and Angerhöfer 1995; Scheunert 1994)

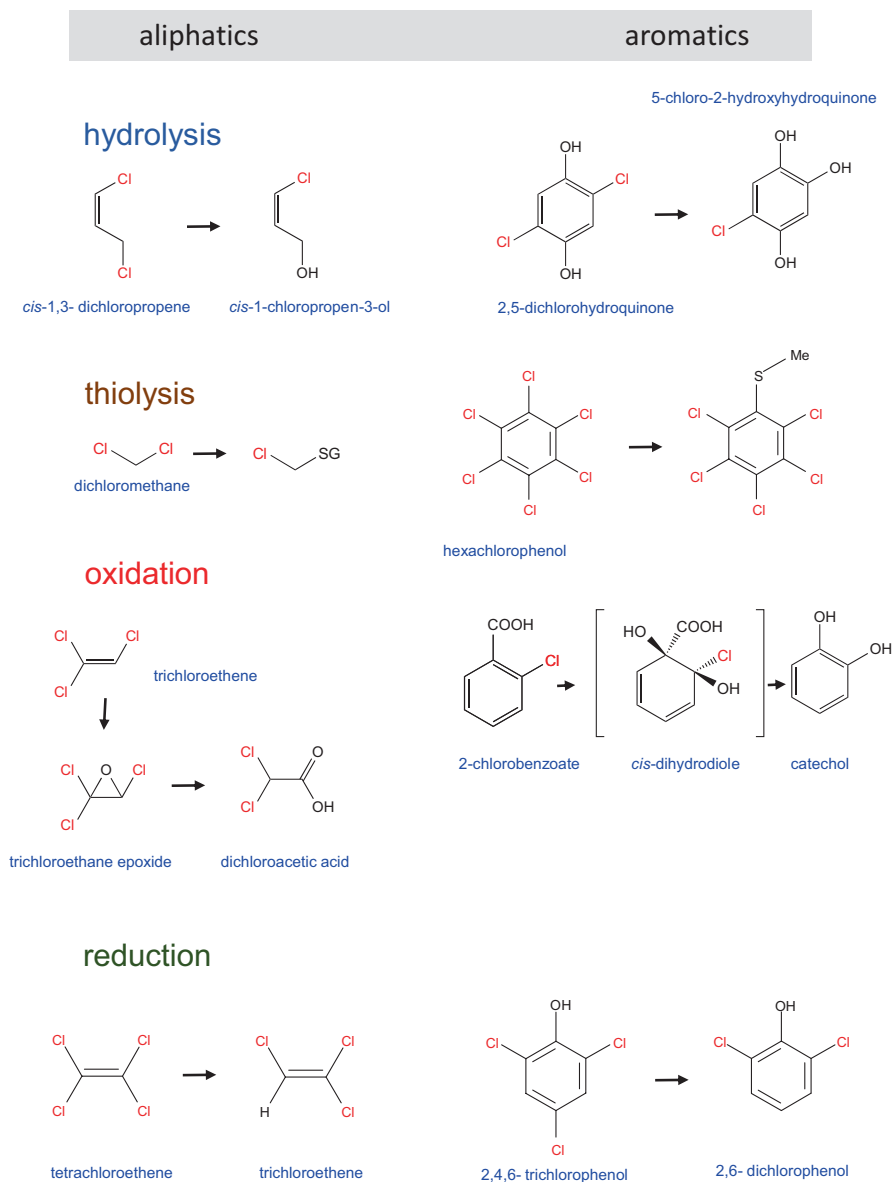


Fig. 1.34 Schematic summary of dechlorination mechanisms (According to Reinecke and Schlömann 2007; Fellenberg 1990; Parlar and Angerhöfer 1995; Scheunert 1994)

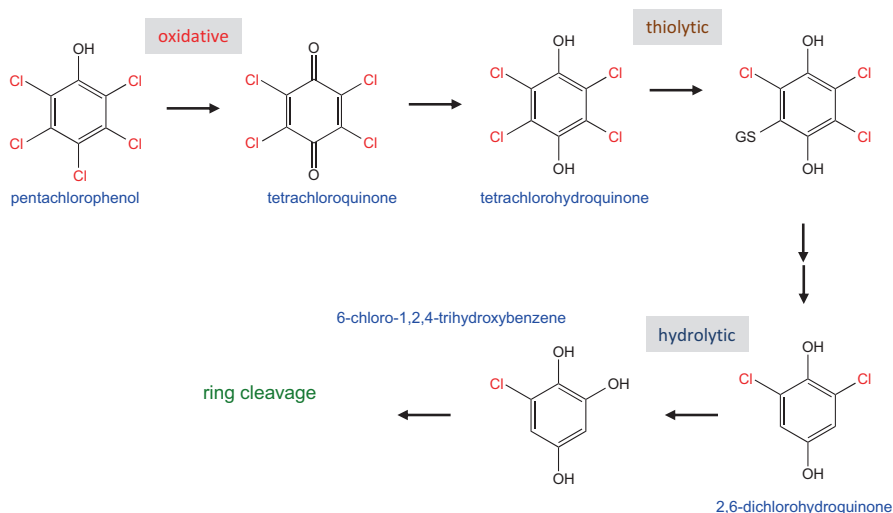


Fig. 1.35 A dechlorination pathway of pentachlorophenol comprising hydrolytic, thiolytic and oxidative mechanisms (According to Reinecke and Schlömann 2007)

carbon atoms. Slight differences exist depending on the point of the first oxidation step (see Fig. 1.36). Terminal oxidation shortens the side chains by two carbon atoms (AcetylCoA) in one oxidation step. Oxidation in 2-position forming first methyl ketones leading to the formation of an acetic acid ester via rearrangement and the subsequent loss of a C_2 -moiety. The cleavage of aliphatic ring systems follows the same reaction pathway as this mid chain oxidation mechanism.

In any case, branching points, in particular irregular ones, often hinder a fast shortening. Here, also a slight variation can be observed. E.g. for isoprenoid type alkanes the degradation is performed via the loss of both C_2 and C_3 units as a consequence of the methyl substitution (see Fig. 1.36).

Noteworthy, anaerobic alkane degradation needs a more complex activation prior to shortening processes and appear generally much slower as compared to aerobic degradation.

The degradation of aromatic hydrocarbons is focused on the cleavage of the stable aromatic ring system. Under aerobic conditions the phase I reactions attach hydroxy groups at the aromatic system leading on the one hand to a higher water solubility but on the other hand to a destabilization of the aromatic ring near the polar groups, respectively (see Fig. 1.37). The number of added hydroxyl groups depends on the enzyme systems available, either mono- or dioxygenase. After activating the ring system cleavage can occur between two polar groups which represents the so-called *ortho*-cleavage. The alternative disjunction nearby the hydroxyl group is called *meta*-cleavage. All resulting fragments can easily be transferred into natural products and integrated into the main metabolism pathways.

This principle degradation pathway is valid also for polycyclic systems including substituted derivatives as illustrated for phenanthrene and a low-chlorinated biphe-

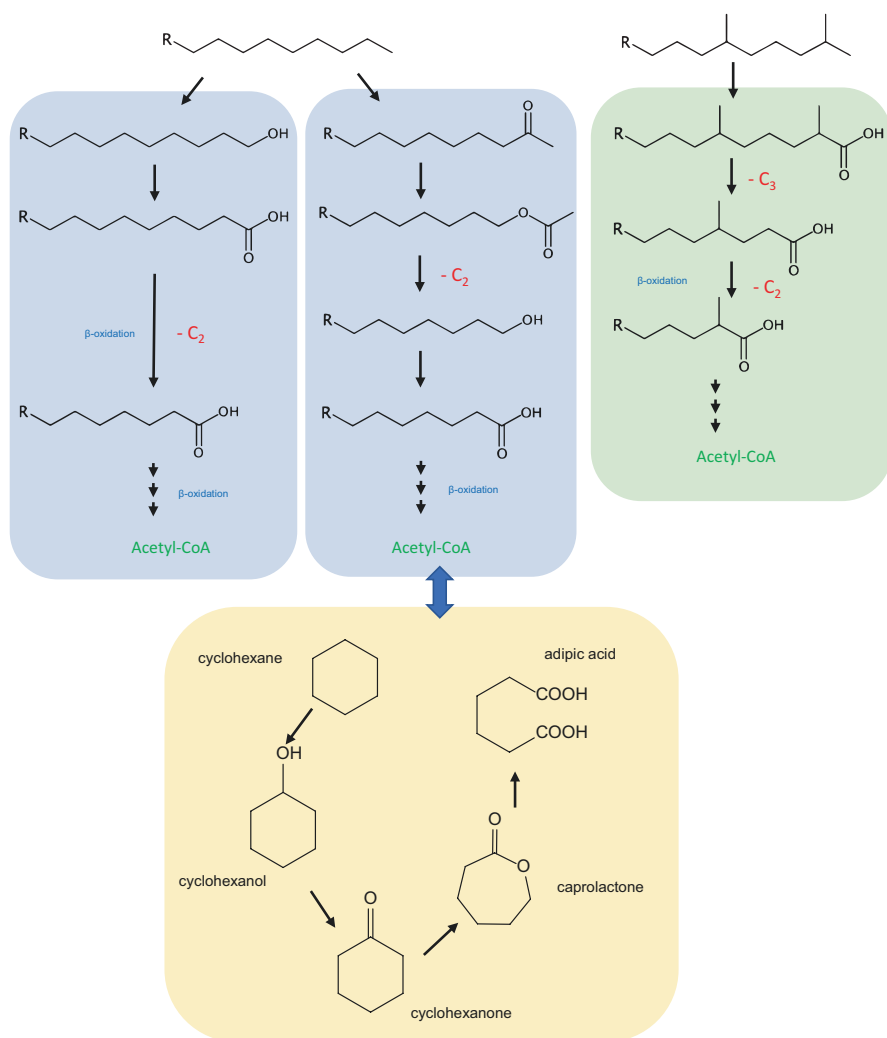


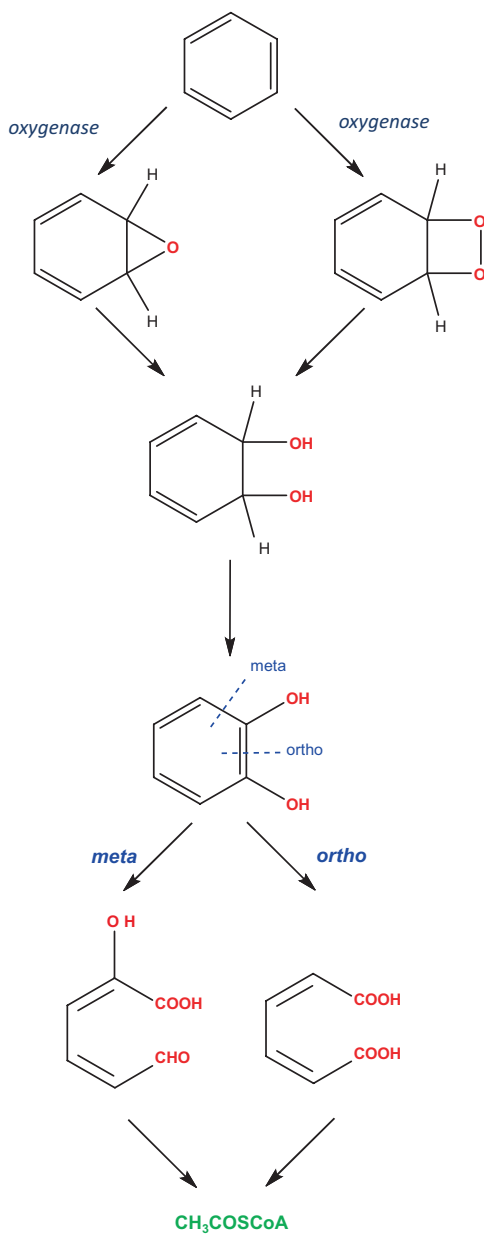
Fig. 1.36 Principal degradation pathways of aliphatic compounds (Modified after Reinecke and Schlömann 2007)

nyl in Fig. 1.38. In case of polycyclic systems, a successive cleavage of all rings can be observed.

Finally, it has to be noted that the degradation pathways of aromatics are highly influenced by substitution in terms of the type of substituent and the position. Often, substituents hinder at a certain step further degradation as illustrated in Fig. 1.39 for chlorinated aromatics.

With respect to anaerobic conditions, the aromatic systems become often hydrogenated. This reaction is preferred for activated aromatic systems (e.g. benzoic acid, phenol etc.). Hydrogenation of aromatics needs energy since it is the reverse reac-

Fig. 1.37 Initial degradation steps for aromatic systems under aerobic conditions (Simplified after Reinecke and Schlömann 2007; Scheunert 1994)



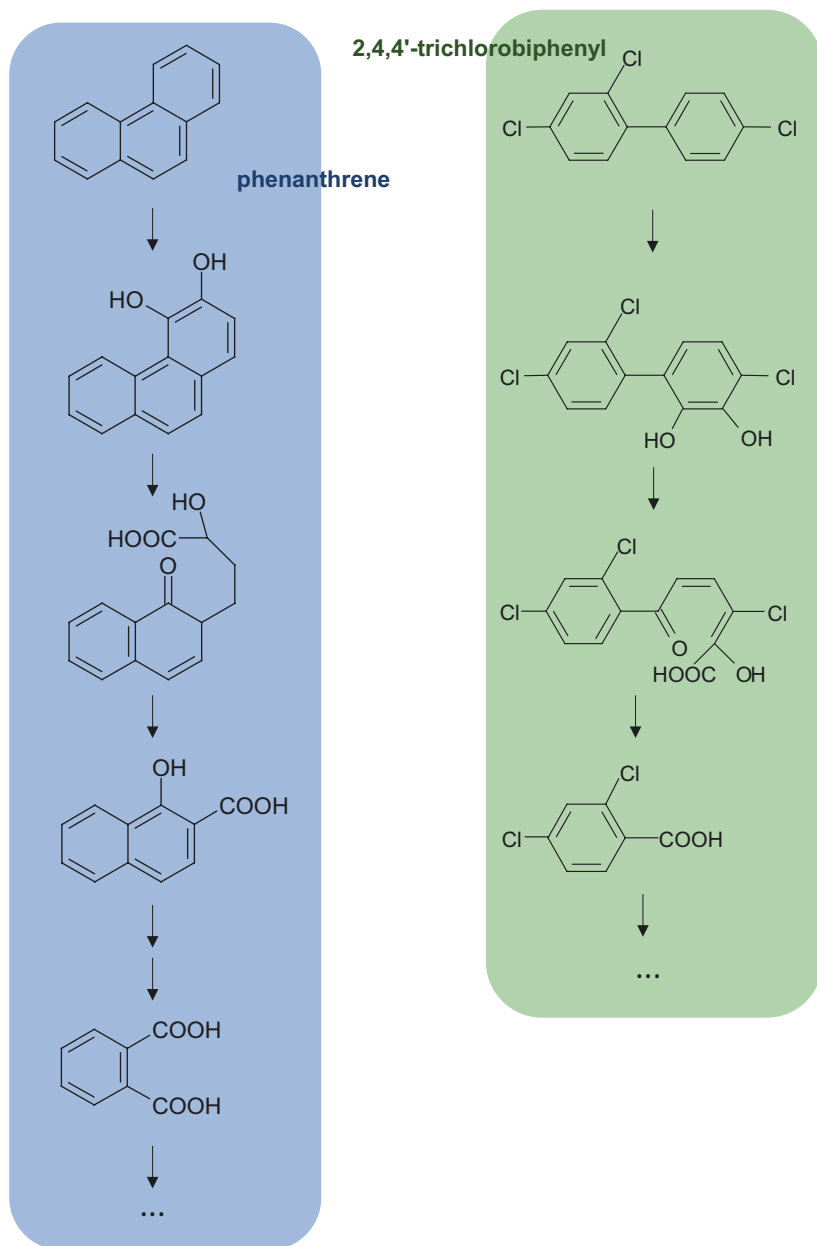


Fig. 1.38 Examples for ring cleavage in annulated and substituted aromatics (Simplified after Reinecke and Schlömann 2007; Scheunert 1994)

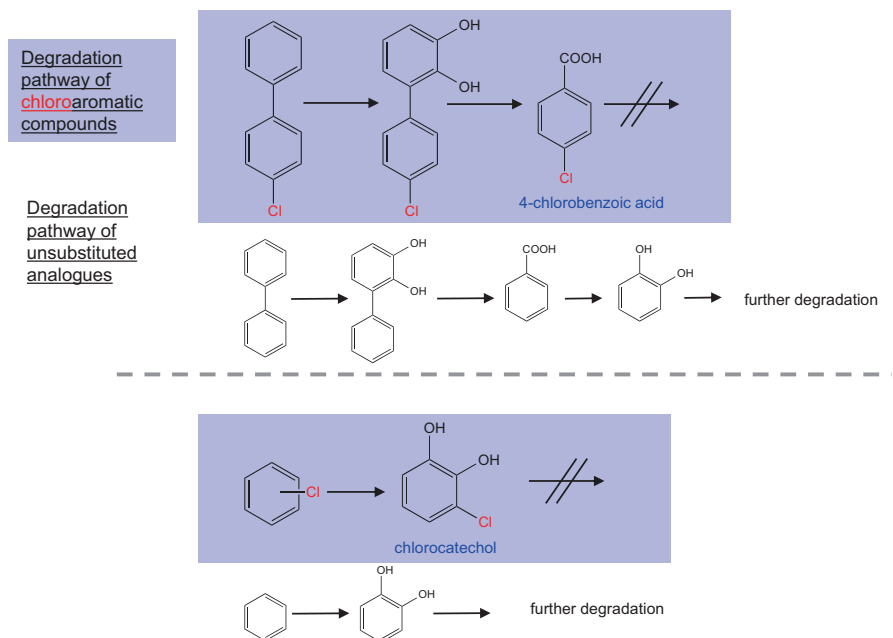


Fig. 1.39 Comparison of degradation pathways of chlorinated aromatics and its non-substituted analogues (Simplified after Reinecke and Schlömann 2007)

tion to aromatic system formation. Nevertheless, subsequent utilization of the intermediates reveals more energy as compared to the hydrogenation, so that the net reaction gains some energy. An example is given in Fig. 1.40.

General Note

The environmental transformation of organic pollutants has to be distinguished for biotic and abiotic but also for aerobic and anaerobic conditions. Secondly, the reaction type should be understood namely oxidation, reduction, hydrolysis, photolysis etc. A complete degradation pathway consists of several steps and sometimes changing conditions are needed for a mineralization.

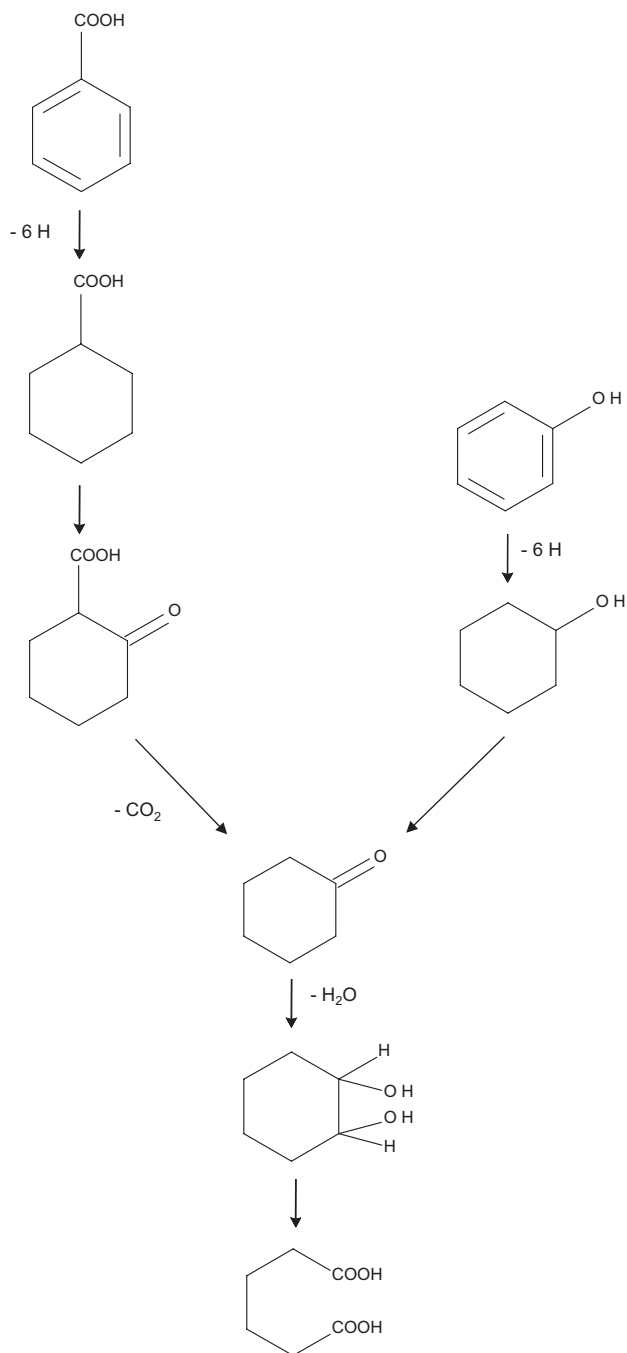


Fig. 1.40 An anaerobic degradation pathway of aromatics (Simplified and modified after Parlar and Angerhöfer 1995)

1.4 Organic Pollution in Hydro-, Pedo- and Atmosphere

Outlook

Despite the principle mechanisms responsible for the environmental fate of organic pollutants, there are also some more specific aspects in the three main compartments pedosphere, hydrosphere and atmosphere. These aspects will be briefly presented here.

Keywords Soil • Groundwater • Air • Surface water • Plants

Organic pollutants in the pedosphere are subjected to various processes effecting their amount and distribution. All these principles are already discussed in Sects. 1.2 and 1.3 and illustrated in Fig. 1.41. However, in soil systems there are two major aspects that are more specific and are needed to be considered, the rhizosphere and the close linkage to groundwater systems.

Soils can be divided into two different parts with respect to its connection to groundwater, the unsaturated and the saturated zone. This differentiation is relevant for the transfer and transport as well as the transformation processes. The transfer of organic contaminants in the unsaturated zone appears between soil air, soil water and the particulate matter, whereas in the saturated zone a transfer occurs mainly between groundwater and soil particles. Further on, a vertical transport through the unsaturated zone and a horizontal transport in the saturated zone along the groundwater flow direction, both triggered by convection, are evident. A differentiation between the unsaturated and saturated zone needs to be considered also with respect to the transformation and degradation processes, since the unsaturated zone is characterized by more aerobic conditions, whereas the saturated zone is mainly anaerobic. Consequently, the microbial community and the resulting transformation pathways differ in both zones. As the most relevant aspect, groundwater contamination is closely linked to soil pollution. This is evident e.g. for the impact of agricultural activities on both soil and corresponding groundwater e.g. by pest control or fertilizer application leading to pesticide and nitrate contaminations by leaking from contaminated top soil layers towards aquifers.

As a second important aspect, plants and especially their roots influence the fate of organic contaminants in soils. There is a high interaction between the root systems and the soil particles resulting in uptake of organic and inorganic substances (e.g. nutrients and water). This root-soil system is also named rhizosphere. In particular, the microbial activity is elevated in the rhizosphere influencing not only the uptake but also the transformation of organic substances. Both uptake and transformation have been used for developing remediation approaches based on plant-soil interaction, the phytoremediation. Depending on the plant species, the pollutants and the soils, three different measures are used (see Fig. 1.43). The phytoextraction accumulates soil pollutants in the plants that are subsequently harvested for eliminating the pollution. This approach is mainly appropriate for heavy metal contaminations. Phytodegradation directly enhances the transformation and degradation of

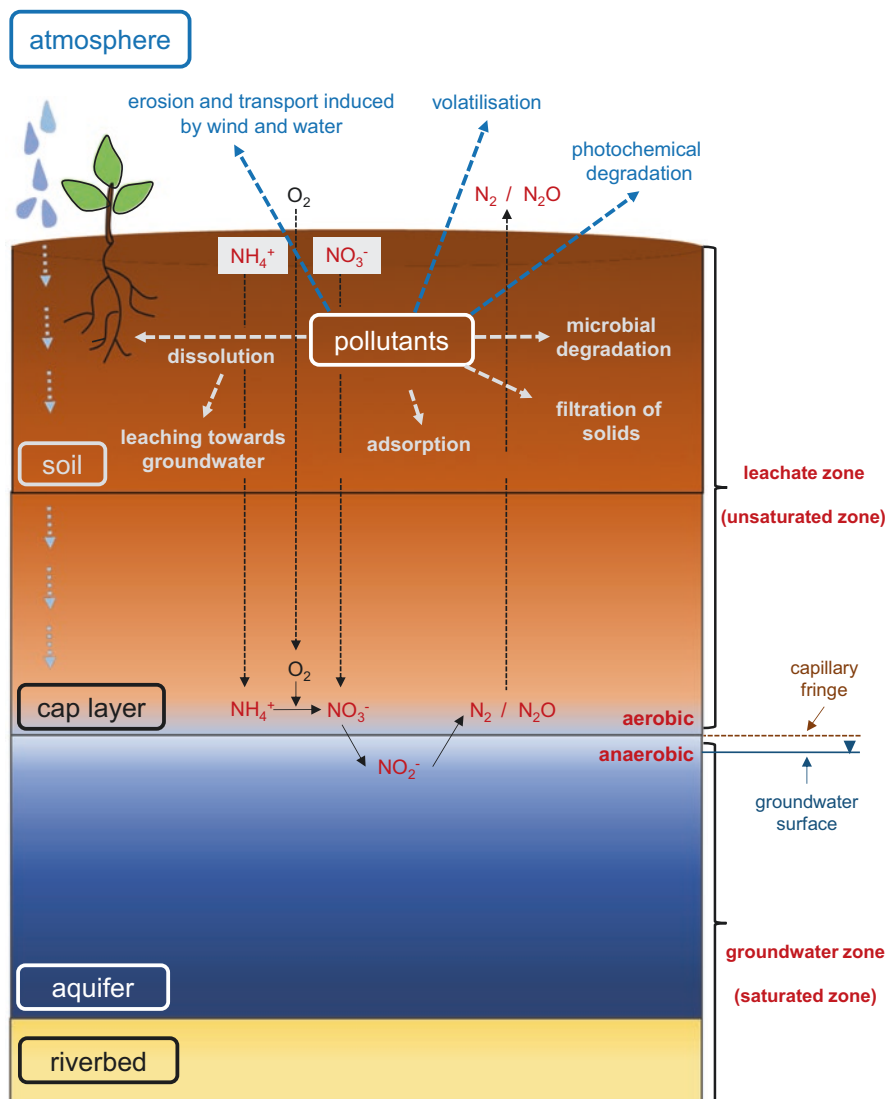


Fig. 1.41 A general scheme of the environmental fate of organic contaminants in soil systems (Modified and expanded after Heinz and Reinhardt 1991; Bliefert 1997)

pollutants either in the rhizosphere or after taking up by plants. These measures are often used for organic pollutants (Fig. 1.42).

Environmental aspects of organic pollutants in the hydrosphere are mainly focussed on surface water systems since groundwater is linked more to soil pollution, as already pointed out. In surface water systems the water body, the sediments and the suspended particulate matter as well as the interface to the atmosphere have

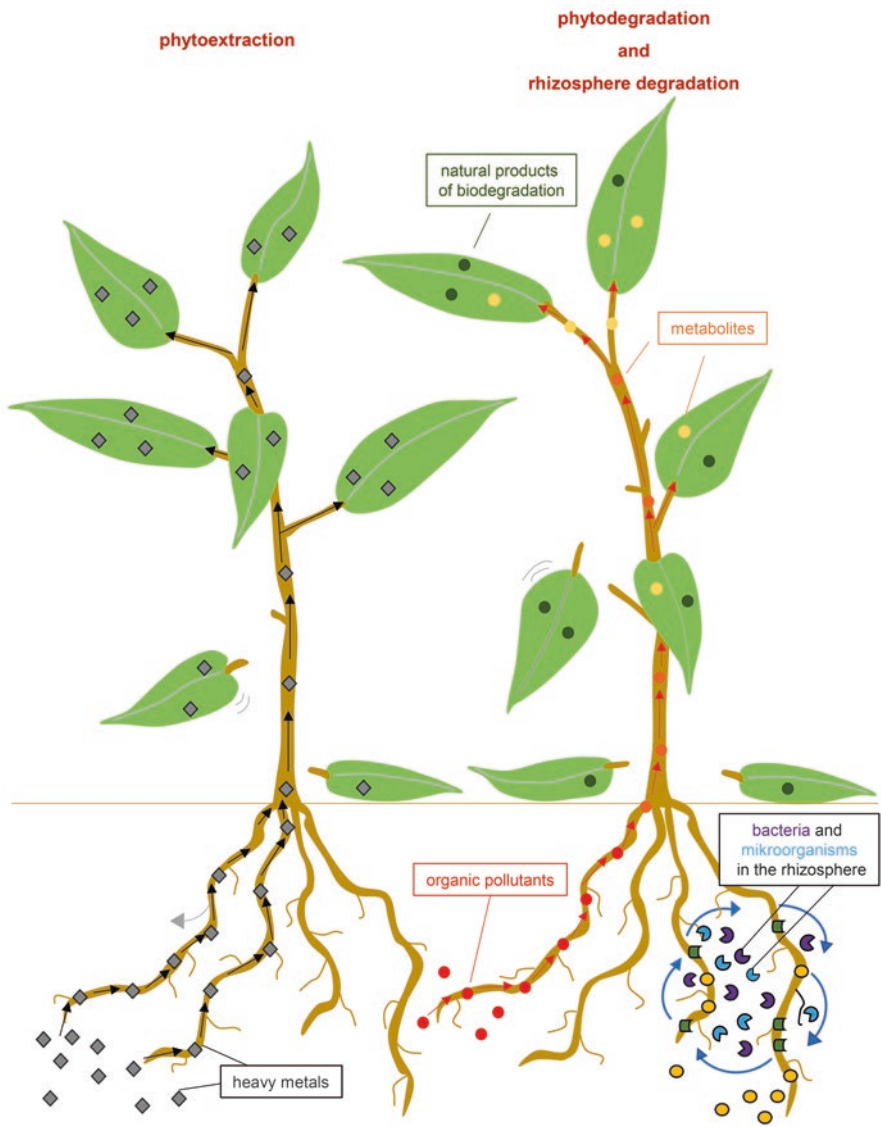


Fig. 1.42 Principal phytoremediation approaches (Modified and simplified after Reinecke and Schlömann 2007)

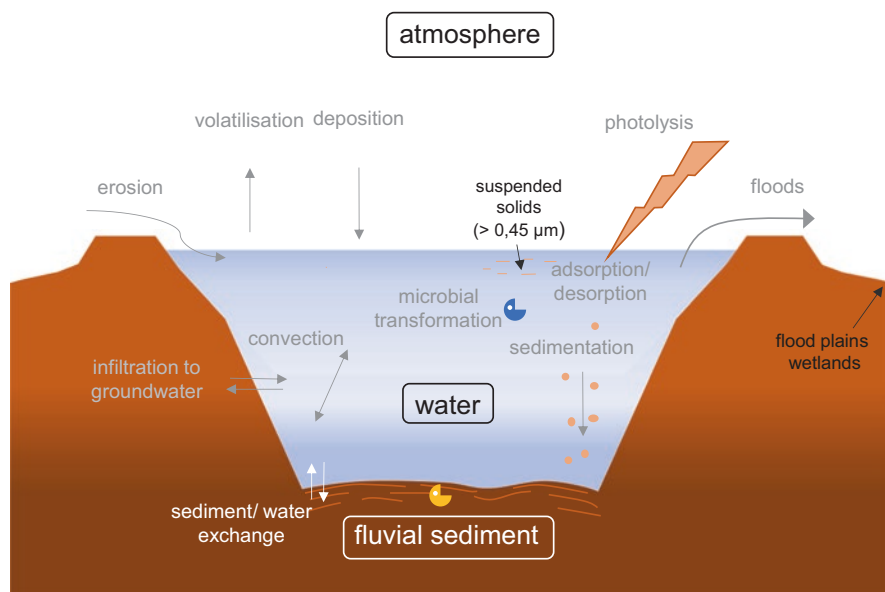


Fig. 1.43 Transfer processes in river systems (Simplified and modified after Schwarzenbach et al. 1993 and Fent 2013)

to be considered for transfer processes. In the water body itself adsorption and desorption of pollutants to and from suspended particulate matter (SPM) is accompanied by sedimentation and remobilisation of these particles according to different flow regimes. As a consequence, a very dynamic exchange and transfer between aqueous and particulate phase is obvious. Additionally, transport is an important aspect for river systems due to partly high flow rates. Here, a transport as dissolved species and in a particle associated way can be differentiated. In the marine environment and in lakes this aspect is of minor importance due to the very low to even not existing water flow. A detailed view on the transfer processes in a river system is given in Fig. 1.43.

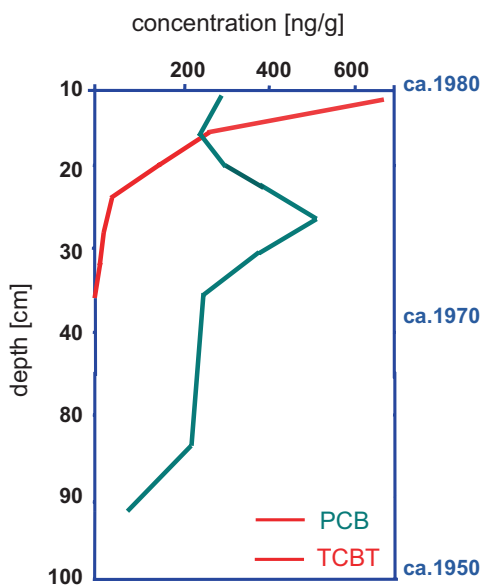
As a specific aspect in river systems the output of riverine material by flood events has to be mentioned. Such events can provoke a transport of riverine particles and their associated pollutants to terrestrial areas where they are deposited on these flood plains or wetlands with significant amounts. In this way, a transfer of aquatic pollution towards soil systems becomes evident.

These floodplains have also an interesting role in a second specific aspect for aquatic ecosystems. Due to the enhanced stability of particle associated organic pollutants and due to the specific characteristic of sedimentation, aquatic systems exhibit the potential to build up geochronological archives.

Principally, pollution histories of persistent and particle bound contaminants can be reconstructed from aquatic sediment archives, if some essential criteria concerning the sediment deposits have been taken into account. In particular, suitable (aquatic) sediment archives request an undisturbed sedimentation preferentially of fine-grained particles during periodic or aperiodic/steady deposition. These conditions are matched by flood plains but also by aquatic sedimentation areas such as marine (e.g. in estuarine areas) or lake deposits, as well as anthropogenically built sediment traps like harbours or water supply dams. The pollutants that can be followed in such archives need to be lipophilic and environmental stable in order to have an enhanced adsorption to particles and no interferences by degradation processes. However, if all preconditions are fulfilled, the pollution history of up to the last 200 years can be monitored. An example is illustrated in Fig. 1.44.

For the last main compartment, the atmosphere, only very few specific aspects have to be highlighted with respect to organic pollution (see Fig. 1.45). Firstly, in this compartment the abiotic degradation processes are of higher importance. In particular, photolysis induced by sun light is a major process of degradation. As a second aspect, the half life time of pollutants in the atmosphere is generally much shorter as compared to the hydrosphere or pedosphere. And lastly, pollutants emitted to the air are hindered to spread easily to all heights in the atmosphere. Changing temperature gradients and so-called pauses at the reversal points lead to the formation of different delimited layers (from the earth's surface: troposphere-stratosphere-mesosphere-thermosphere). Between these layers the passage of substances is very restricted due to a diffusion-reduced barrier. Consequently, the dominant amount of pollutants is emitted in the troposphere and remains here. If fractions of stable contaminants are able to pass slowly the

Fig. 1.44 Example of a geochronological study revealing the pollution history of the Lippe river (Germany) reflecting the substitution of polychlorinated biphenyls (PCBs) by tetrachlorinated benzyltoluenes (TCBT) beginning ca. 1970 in the coal mining industry at the Ruhr basin (Data from Heim et al. 2004)



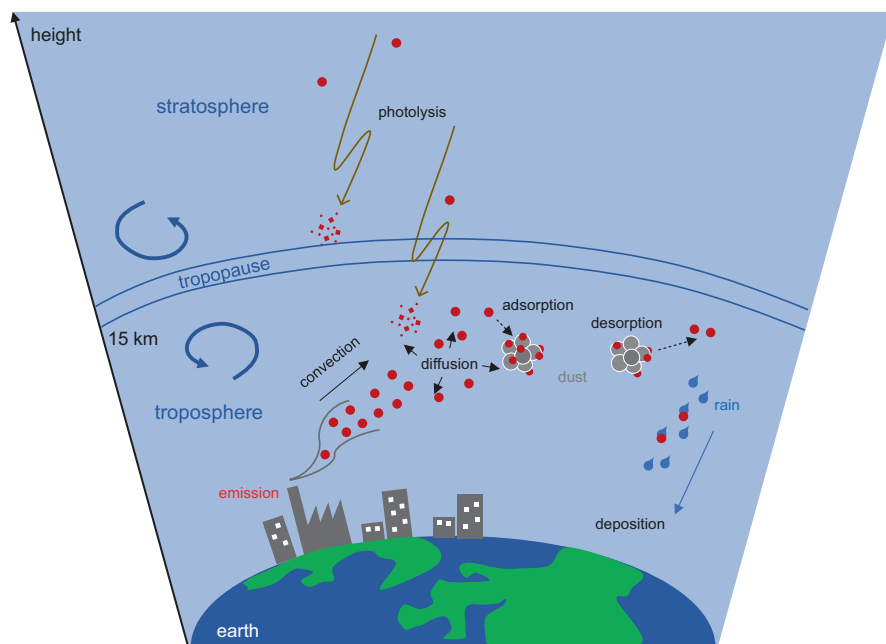


Fig. 1.45 Scheme of principal processes in the atmosphere environmentally relevant for organic pollutants

tropopause they remain in the stratosphere for a prolonged time. This effect is a very important aspect for the harming impact of chlorofluorocarbons CFC on the ozone layer (see Sect. 2.2).

General Note

All the major environmental compartments exhibit specific conditions and subsystems, that influence intensively the principle environmental pathway of pollutants. This specificity needs to be considered in any environmental assessment of pollutants.

1.5 Bound Residues

Outlook

Organic contaminants released to soils or sediments can form non-extractable residues (NER) also known as bound residues. This formation but especially the environmental implications are discussed here.

Keywords Non-extractable fraction • Bioavailability • Aging • Adsorption • Covalent linkage • Humic substances

First evidence for the formation of non-extractable residues in soils was made in the 1940s by investigating the fate of pesticides after application to agricultural soils. For this purpose, ^{14}C -labelled substances have been applied to soils as incubation experiments. With this approach, the mass balance based on the measured radioactivity discriminates the mineralized proportion (determined by $^{14}\text{CO}_2$), the remaining but available fraction of parent compounds including metabolites and, as a third fraction, the non-extractable residues. The behavior of pesticides has been investigated to evaluate the effectiveness of their application, because bound pesticides provide no effect on pests. This motivation points to one highly relevant aspect of bound residues. Bound substances are not available, in particular they are not bioavailable. Hence, formation of bound residues lowers the (eco)toxic potential of pollutants. Contrarily, the bound compounds are also not accessible for biotic degradation or transformation. Hence, bound residues effect both a higher environmental stability and a lower (eco)toxicological impact (see Fig. 1.46).

The process of bound residue formation is dynamic and partly reversible. The quality of incorporation changes with time, which is part of the so-called aging (see

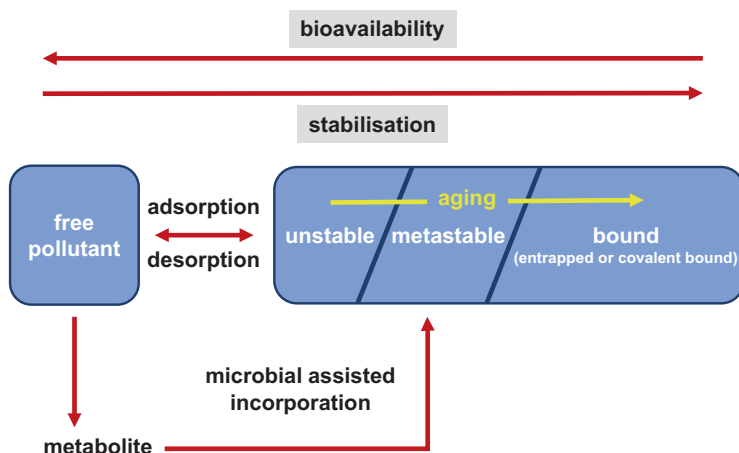


Fig. 1.46 Principles and effects of bound residues formation

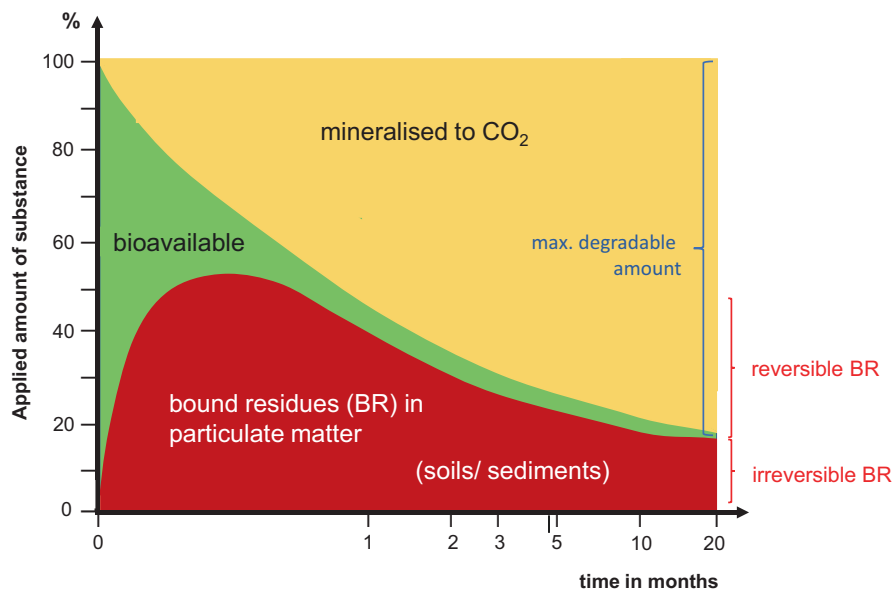


Fig. 1.47 Scheme for long term behavior of bound residues and corresponding bioavailable and mineralized fractions of organic contaminants (Modified after Heinz and Reinhardt 1990)

Fig. 1.46). Noteworthy, the free available proportion is influenced by the immobilization and later remobilization of contaminants and the mode of incorporation. The long-term fate of bound residues and its implication for the bioavailable fraction can be illustrated by a simple scheme (see Fig. 1.47). Here, a first increase of bound residues formation is associated with ongoing mineralization and a sharp decrease of the bioavailable fraction. After a maximum of bound residue formation, this fraction decreases slowly as result of remobilization processes. The deliberated proportion is now subject to biodegradation and finally mineralization. However, the amount of bioavailable substances is triggered by the remobilization rate from bound residues and the mineralization or degradation rate. Finally, the bound fraction converges to a constant level representing the irreversible bound fraction.

Systematic investigations revealed for nearly all pesticides the potential to form such bound residues but in highly varying proportions (see Fig. 1.48). However, the formation of bound residues is not restricted neither to pesticides nor to soils. A wide range of organic substances forms bound residues in soils but also in sediments.

The mode of incorporation can be roughly divided into three different types. These interactions are located at different sub compartments in soil or sediment particles. Very roughly, soil particles consist of a mineral core covered partly by organic matter (dominantly humic substance type material) as well as biofilms produced and stabilized by microorganisms (see Fig. 1.49).

Pesticides

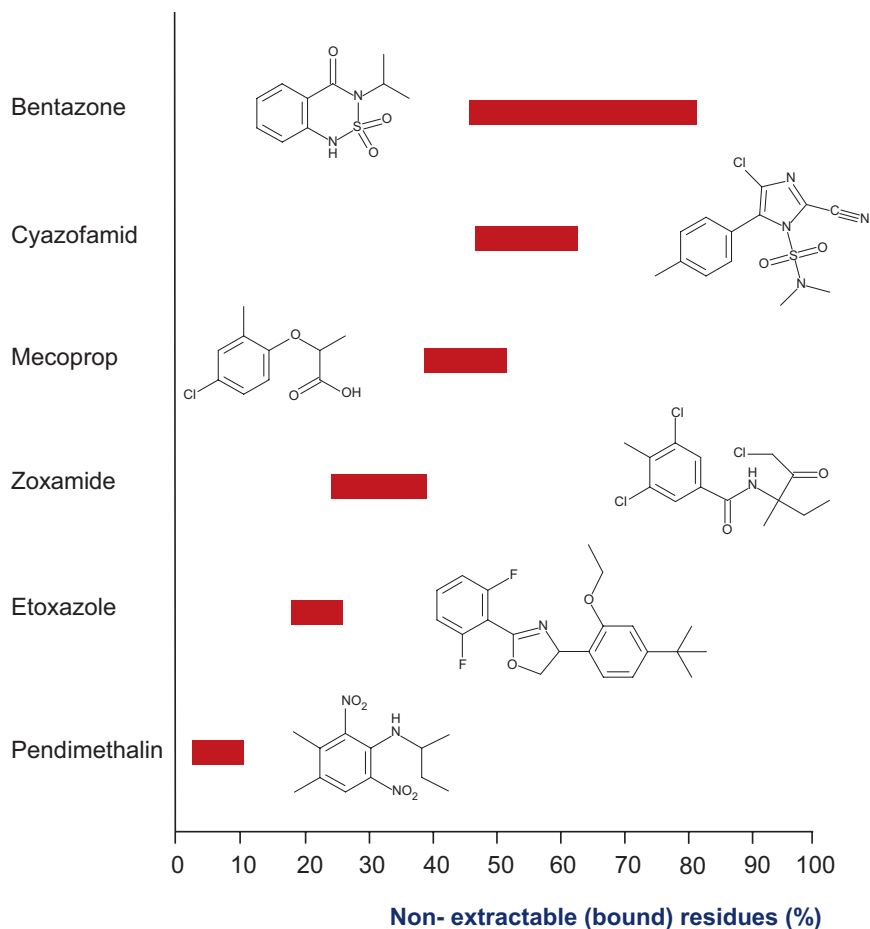


Fig. 1.48 Bound residue fractions of different pesticides in soils (Adapted from and simplified after Barriuso et al. 2008)

A first type of incorporation represents stronger adsorption on organic matter but also to a high extent on clay minerals, in particular in their pore structures (see Fig. 1.50). Here, the immobilization and especially the remobilization is dominantly influenced by the diffusive processes within the pores. The migration into pores but especially the remobilization out of the pores can be a long time process but is reversible. A huge proportion of bound residues especially of non-functionalized organic substances (e.g. PAHs) are bound by this type of incorporation. The basic interactions at the particle or pore surfaces are van-der Waals forces, charge transfer complexes, dipole interactions and related non-covalent linkages.

A principally different type of bound residue formation are covalent linkages that chemically incorporate organic substances with functional groups. Here, reactions

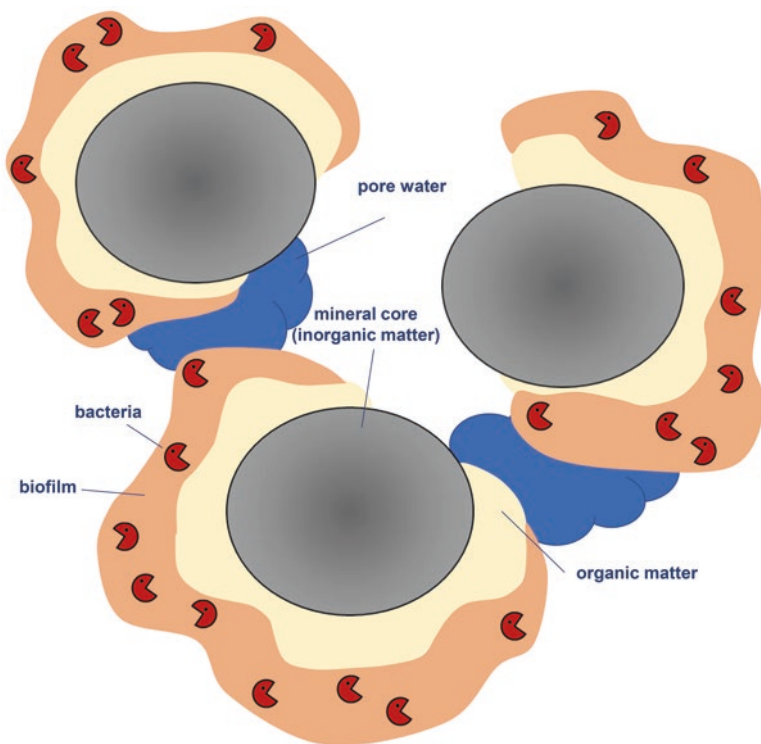


Fig. 1.49 Principal micro composition and structure of soils

with the soil or sediment organic matter is the main process. This natural organic matter, dominantly consisting of humic substances and degraded biomolecules such as polysaccharides or lignine, is structurally not fully understood but some characteristics are evident. Important functional groups are carboxylic and hydroxy groups, but also amino and carbonyl functionalities have been identified. An ongoing debate about the size and nature of soil organic matter contrasts either a macromolecular structure with a variety of irregular connected but multifunctional moieties or an association of more middle-sized molecules with a strong intermolecular aggregation, that behave like macromolecules. One idea about the chemical network of this natural organic matter is illustrated in Fig. 1.51.

However, it is obvious that a lot of chemical reactions between low molecular pollutants and such type of organic matter are possible. On the one hand, reversible incorporation via esters or amides linkages are described, e.g. for phenolic or acidic components. But also irreversible incorporation can occur leading to bound residues that are finally deposited in the particulate matter. Knowledge about the further environmental fate of such residues is very limited. This is partly related to the difficulties in analyzing such bound residues. In particular, an unambiguous identification of covalent linkages of non-extractable residues is difficult. Spectroscopic

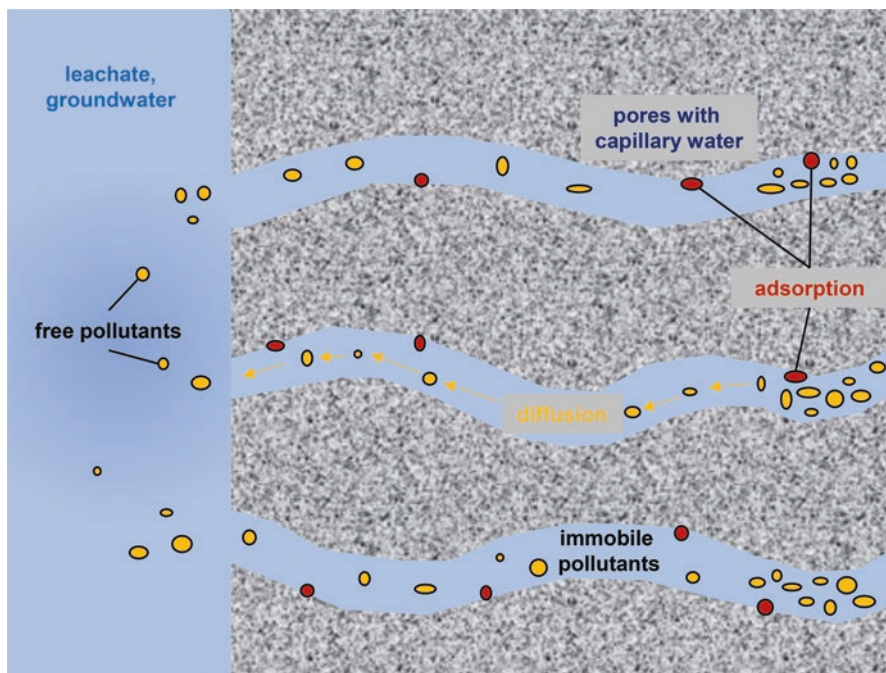


Fig. 1.50 Scheme of reversible incorporation mechanism based on non-covalent interaction

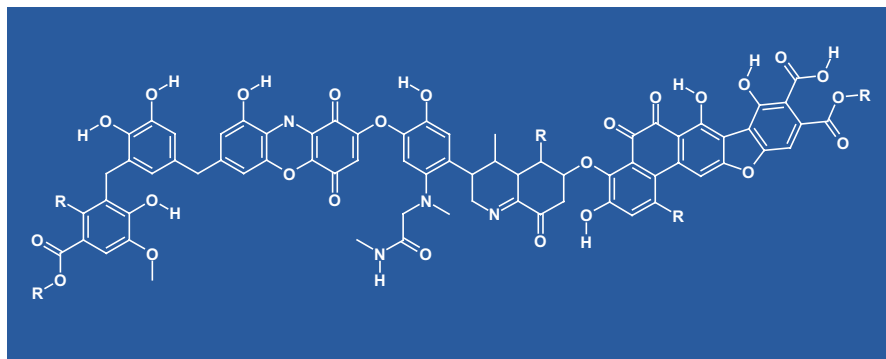


Fig. 1.51 Structural idea of natural humic substances

methods detecting the linkages *in situ* (as non-destructive methods) need special conditions (e.g. an enrichment of ^{13}C for NMR spectroscopy) which prevent a direct measurement of natural systems. This approach can be better used in incubation experiments. Alternatively, the linkages (in particular in case of reversible incorporations) can be cleaved via chemical or pyrolytic degradation and the resulting products can be analysed by standard methods (e.g. gas chromatography coupled with

Fig. 1.52 Overview on principal analytical approaches for characterizing covalently bound residues (see also Northcott and Jones 2000)

Analytical methods for structural characterisation of geogenic macromolecules and bound residues	
non-destructive	destructive
Spectroscopy	Pyrolytic and chemical degradation
Spiking experiments/ labelled substances	Analysis of natural systems

mass spectrometry GC/MS). However, here a clear evidence for covalent bonds is missing because also physical incorporation can be deliberated by such degradation techniques. Both approaches are briefly summarized in Fig. 1.52.

General Note

The formation of bound residues represents an important aspect in environmental risk assessment of organic pollutants applied to soils and accumulated in aquatic sediments. Reduced bioavailability but also prolonged stability and a potential for secondary emissions need to be considered here. As a second important aspect, the reversibility of some types of bound residues has to be considered in environmental risk assessments.

Excursus – Analytical evidence for covalent linkage of bound residues

As mentioned above the unambiguous analysis of covalently bound compounds is very difficult since one has to demonstrate clearly that a linkage has been formerly formed. A smart possibility is the usage of labelled chemicals in chemical degradation reactions. This has been applied to identify a covalent incorporation of the acidic DDT metabolite DDA by hydrolysis with ^{18}O -labelled water and subsequent identification of incorporated ^{18}O in the released pollutant. This approach is illustrated below.

(continued)

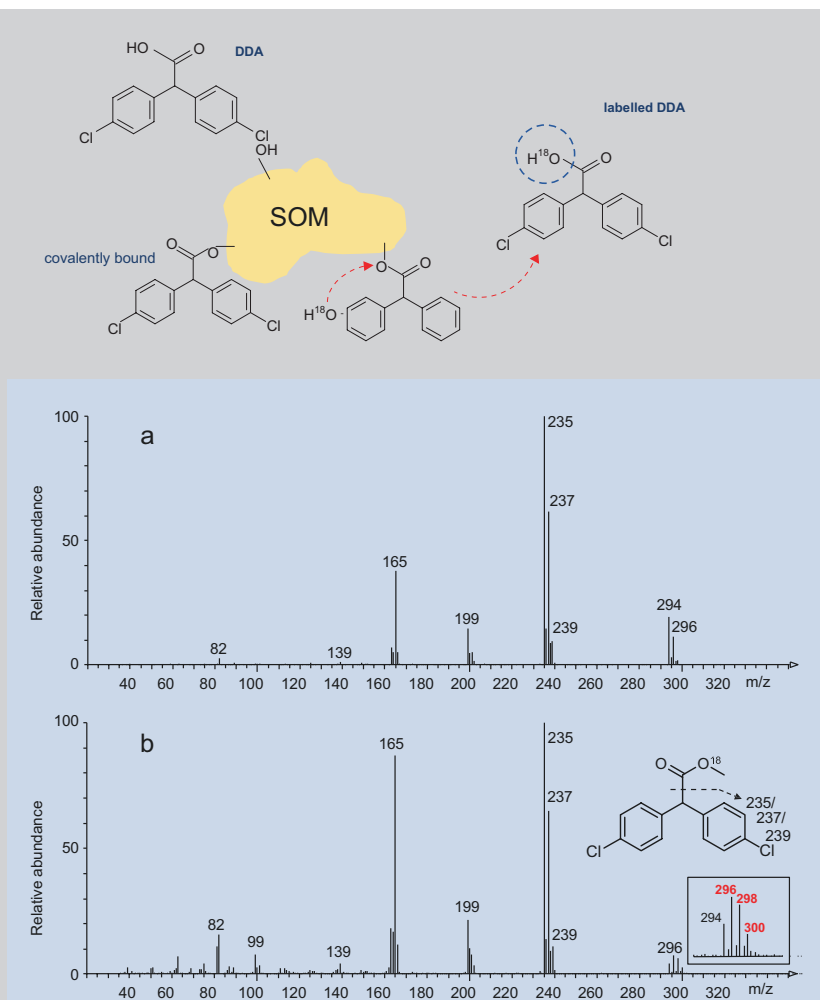


Figure: Hydrolysis of reversible incorporated DDA from sediment organic matter by labelled H_2^{18}O and subsequent detection by GC/MS (Adapted and modified from Kalathoor et al. 2015)

References

- Alloways BJ, Ayres DC (1996) *Schadstoffe in der Umwelt*. Spektrum Akademischer Verlag, Heidelberg
- Barriuso E, Benoit P, Dubus IG (2008) Formation of pesticide nonextractable (bound) residues in soil: magnitude, controlling factors and reversibility. *Environ Sci Technol* 42:1845–1854
- Bliefert C (1997) *Umweltchemie*, 2nd edn. Weinheim, Wiley VCH
- Bliefert C (2002) *Umweltchemie*, 3rd edn. Wiley VCH, Weinheim
- Fellenberg G (1990) *Chemie der Umweltbelastung*. BG Teubner, Stuttgart
- Fent K (2013) *Ökotoxikologie*, 4th edn. Georg Thieme Verlag, Stuttgart
- Fritsche W (1998) *Umwelt-Mikrobiologie*. Gustav Fischer Verlag, Jena
- Heim S, Schwarzbauer J, Kronimus A, Littke R, Woda C, Mangini A (2004) Geochronology of a load history: anthropogenic pollutants in riparian wetland sediments of the Lippe river (Germany). *Org Geochem* 35:1409–1425
- Heindel JJ, vom Saal FS, Blumberg B et al (2015) Parma consensus statement on metabolic disruptors. *Environ Health* 14:45
- Heintz A, Reinhardt G (1991) *Chemie und Umwelt*. F. Vieweg & Sohn, Braunschweig
- Kalathoor R, Zeiner M, Schmidt B, Schäffer A, Schwarzbauer J (2015) First evidence for covalent linkage of acidic metabolites of metalaxyl and DDT as non-extractable pesticide residues in soil and sediment. *Environ Chem Lett* 13:431–437
- Kidd KS, Blanchfield PJ, Mills KH, Palace VP, Evans RE, Lazorchak JM, Flick RW (2007) Collapse of a fish population after exposure to a synthetic estrogen. *PNAS* 104:8897–8901
- Northcott GL, Jones KC (2000) Experimental approaches and analytical techniques for determining organic compound bound residues in soil and sediment. *Environ Pollut* 108(1):19–43
- Parlar H, Angerhöfer D (1995) *Chemische Ökotoxikologie*, 2nd edn. Springer, Berlin
- Reinecke W, Schlömann M (2007) *Umweltmikrobiologie*. Elsevier – Spektrum Akademischer Verlag, München
- Rodricks JV (1992) *Calculated risks*. Cambridge University Press, Cambridge
- Scheunert I (1994) Mikrobieller Abbau organischer Fremdstoffe im Boden. *CHIUZ* 28:68–78
- Schwarzenbach RP, Gschwend PM, Imboden DM (1993) *Environmental organic chemistry*. Wiley, New York
- Vasseur P, Cossu-Leguille C (2006) Linking molecular interactions to consequent effects of persistent organic pollutants (POPs) upon populations. *Chemosphere* 62:867–873

Further Reading

- Barracough D, Kearny T, Croxford A (2005) Bound residues: environmental solution or future problem? *Environ Pollut* 133:85–90
- Gevao B, Semple KT, Jones KC (2000) Bound pesticide residues in soils: a review. *Environ Pollut* 108:3–14
- Heim S, Schwarzbauer J (2013) Reconstructing pollution history by geochronology of anthropogenic contaminants in aquatic sediment archives – a review. *Environ Chem Lett* 11:255–270

Chapter 2

Organic Pollutants

Outlook

A wide range of organic substances of anthropogenic origin have been detected in the environment. Many of them are characterized as pollutants pointing to harmful effects and extended environmental stability. Since many environmentally relevant properties of these contaminants are related to both molecular structures and fields of application, important pollutant classes are discussed in detail classified either by their chemistry (e.g. halogenated compounds, PAHs) or their technical application (e.g. pesticides, explosives) in this chapter.

Keywords Chloro-organics • Bromo-organics • Persistent organic pollutants POPs • Congener pattern • Dehalogenation

A wide range of organic substances of anthropogenic origin have been detected in the environment. Many of them are characterized as pollutants pointing to harmful effects and extended environmental stability. Since many environmentally relevant properties of these contaminants are related to both molecular structures and fields of application, important pollutant classes are discussed in detail classified either by their chemistry (e.g. halogenated compounds, PAHs) or their technical application (e.g. pesticides, explosives) in this chapter.

2.1 Halogenated Compounds

Outlook

Halogenated organic compounds represent one of the most important groups of pollutants. Many halogenated aliphatic pollutants are small molecules with relevance for the atmosphere and ground water. Halogenated aromatics exhibit often lipophilic properties and are typical contaminants in particulate matter. Numerous representatives are discussed in this chapter.

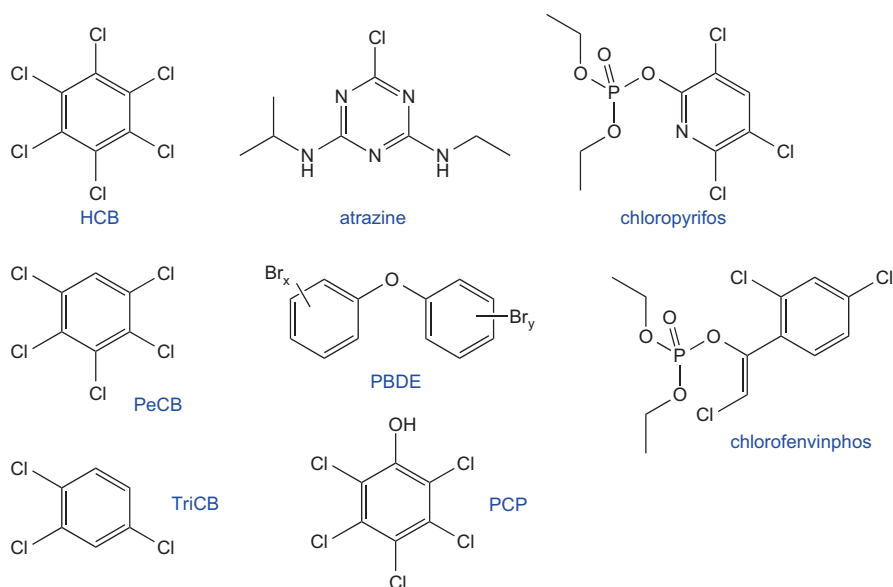


Fig. 2.1 Halogenated compounds appearing in the appendix of the EU Water Framework Directive as priority pollutants

Halogenated organic compounds represents one of the most important groups of pollutants. Many very well-known contaminants like dioxins or CFC belong to this substance class. Main focus was laid in former times to chlorinated pollutants but has been expanded in the last two decades also to brominated, fluorinated and iodine containing compounds. The high relevance of chloro-organic pollutants even in former times is highlighted by an ironic and provoking sentence written by the very well-known environmental scientist Otto Hutzinger in 1990 stating that ‘God created 91 compounds, human beings around a dozen, but the devil just one – chlorine’.

This high environmental interest on chlorinated compounds is based on the high stability in the environment for which many of halogenated organic substances are in the meanwhile classical representatives. The high persistence but also the environmental relevance *per se* is proved amongst others by the dominant occurrence of halogenated compounds in lists of priority pollutants, e.g. the *Dirty Dozen* of the *Stockholm Convention* (see Fig. 4.1 in Chap. 4) or the appendix of the EU Water Framework Directive as illustrated in Fig. 2.1.

From a historical point of view first technical applications and corresponding commercial usage of halogenated organics dates back to the beginning of the last century (see Fig. 2.2). Many common products such as PER (tetrachloroethene), PVC (polyvinylchloride) or PCB (polychlorinated biphenyls) have been introduced to the market in the 1910s and 1920s. Noteworthy, scientific interest and a systematic investigation of the environmental impact of such contaminants started first in the beginning 1960s initiated *inter alia* by the publication of Rachel Carsons’ book ‘Silent Spring’.

At the beginning of environmental studies on halogenated contaminants it has been partly mentioned that the stability especially of chlorinated compounds was based on a general miss of natural halogenated compounds and, consequently, the

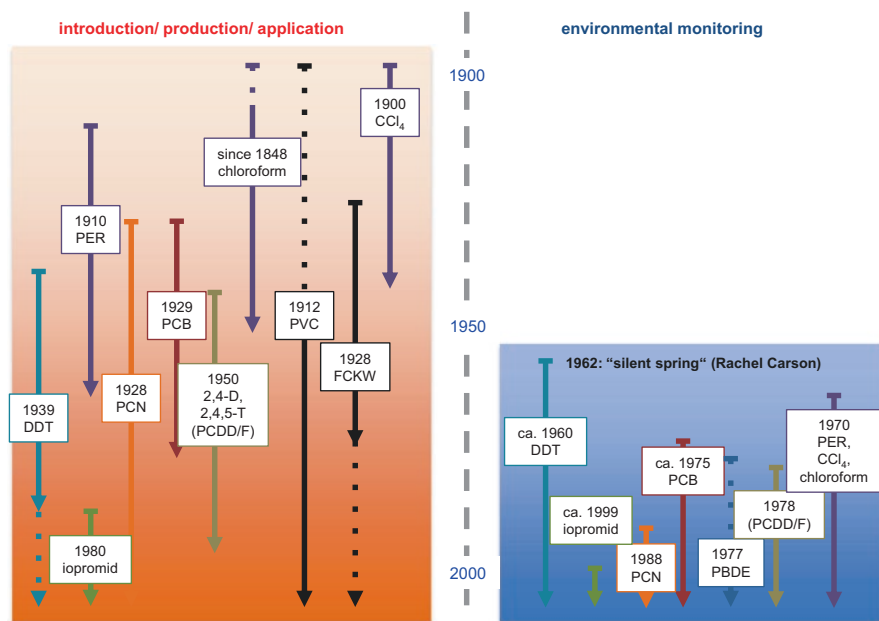


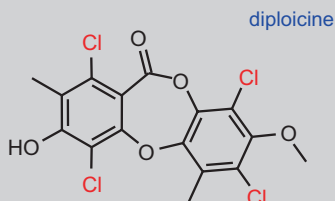
Fig. 2.2 Historical comparison of production and usage of selected halogenated compounds with their environmental monitoring (Modified after Schwarzbauer 2005)

lack of microbial tools for attacking the carbon-chlorine bonds. However, this assumption was certainly not correct. There are many natural products containing chlorine and bromine as well as iodine. Examples for organisms from various environmental compartments are given in Fig. 2.3.

However, it has to be noted that the interest on halogenated natural products and also the knowledge about them, increased significantly not until the 1970s. This is pointed out in Fig. 2.4 by the number of identified compounds over time, where a clear increase in the time period after 1970 is evident.

Excursus – The first identified chlorinated natural product

The first identification of a chlorinated natural product dates back to the beginning of the twentieth century. In 1905, diploicine was isolated first as natural product, but it needed nearly 30 years till the compound was fully identified (1934). However, diploicine is known as the first natural product containing chlorine, here four atoms.



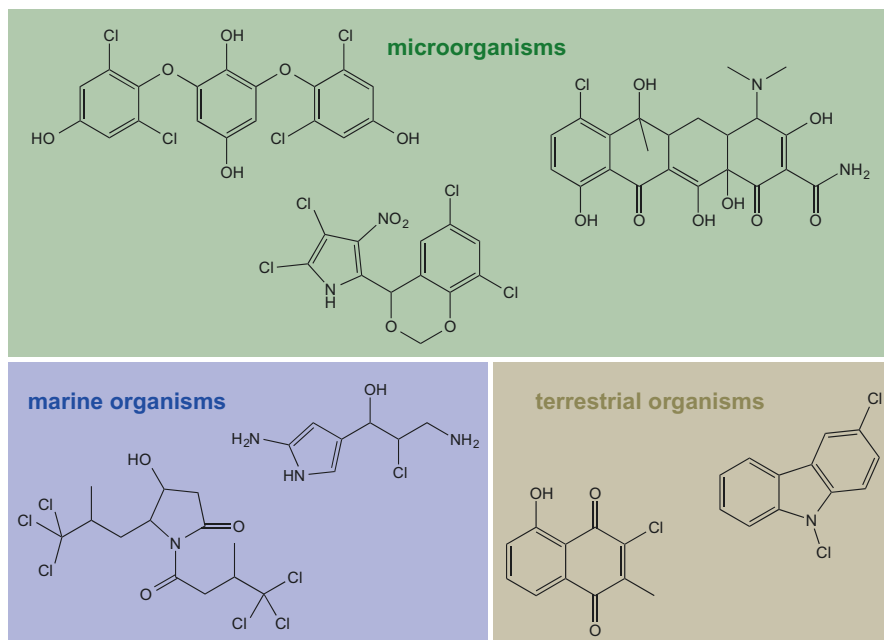


Fig. 2.3 Some examples of halogenated biomolecules from various organisms (According to Naumann 1993, Ballschmiter 2003)

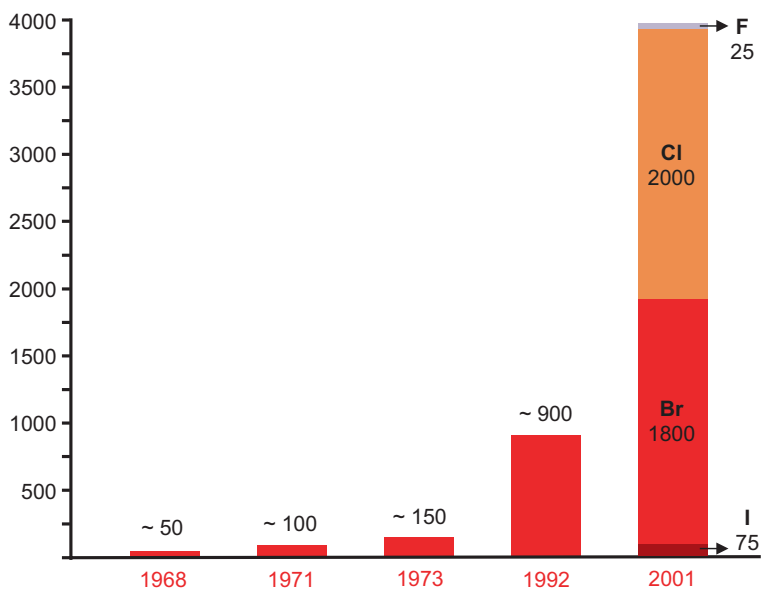


Fig. 2.4 Numbers of known organic compounds containing halogens over time. For 2001 a subdivision according to type of halogen is given (Data adapted from Geckeler and Eberhardt 1995)

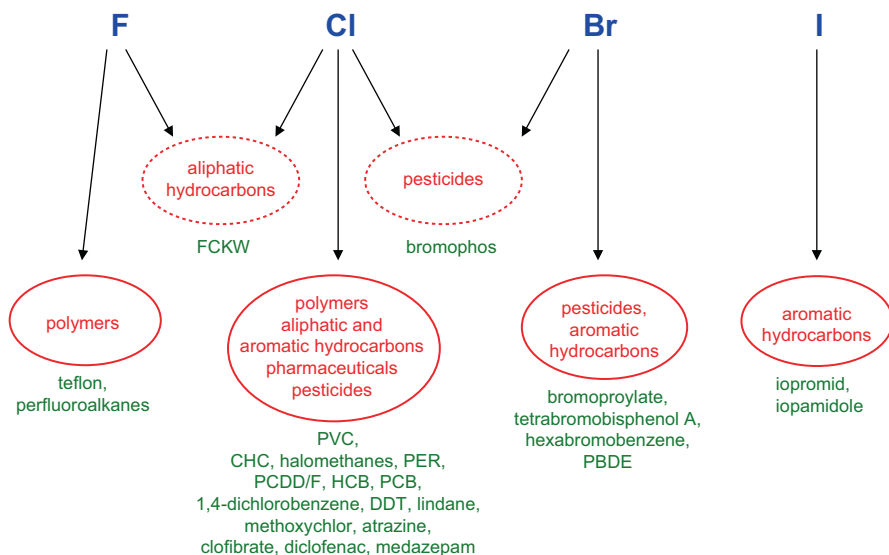


Fig. 2.5 Systematic summary of halogens in technical organic compounds and their corresponding fields of applications as well as representative substances (Modified after Schwarzbauer 2005)

Table 2.1 Concentration levels (ng/g) of selected halogenated pollutants

Sample type	Hexachlorobenzene (HCB)	Polychlorinated biphenyls (PCB)
Soil	6	6
Earthworm	0.1	34
Sewage sludge	1.5	630
Macroalgae	0.04	5
Capers	7	4350
Cow's milk	0.4	15
Breast milk	240	300
Human liver	270	1350
Human fat	1500	10,220

Data adapted from Bliefert (2002)

The usage and application of halogenated compounds is very diverse. Main fields of applications are usage as synthesis intermediates, technical additives or pesticides. But many further, more specialized application areas exist. Applications are somewhat determined by the type of halogens appearing in the xenobiotics. This is exemplified in Fig. 2.5. Noteworthy, also mixed halogenated compounds are used but only to a minor extent.

The broad field of application, the often very high environmental stability and the tendency especially for the halogenated hydrocarbons to geo- and bioaccumulate lead to an ubiquitous appearance of many of such contaminants (see Table 2.1). Several compounds are highly known as representative environmental pollutants,

e.g. dioxins, PCBs or CFCs. Since the field of application as well as the principal chemical properties differ for halogenated aliphatics and aromatics, both groups are discussed separately in the following.

2.1.1 *Halogenated Aliphatics*

Aliphatic compounds are mainly substituted with chlorine and fluorine atoms. Many of them are of low molecular weight and exhibit accordingly an extended volatility. Many organic solvents are halogenated aliphatics.

2.1.1.1 CFC

One very well-known group of environmental highly relevant halogenated aliphatics are the mixed substituted chlorofluorocarbons, CFC. These compounds are commonly perhalogenated methane, ethane and to a minor extent propane derivatives. As a main physico-chemical property, all CFC are volatile to highly volatile. From a technical point of view their low reactivity, comprising also a low flammability, are of high interest. This is due to the highly stable C-F and C-Cl bonds. Further on, CFC exhibit a low toxicity.

These properties lead to the technical applications of CFC which are used as solvents, degreasing agents, propellants but especially as refrigerants. These applications resulted partly in a direct emission of CFC to the environment, in particular to the atmosphere. But also careless usage and accidental release induced an atmospheric pollution. Although the toxicity of these compounds is not high, they exhibit a high relevance due to their chemical reactions in the environment. Once released to the atmosphere they have relatively high half-life times of up to decades and are detectable at trace concentration in the order of 10 to 500 pmole/mole (http://cdiac.ornl.gov/oceans/new_atmCFC.html). Further on, as a result of their properties they are able to pass to a low extent the tropopause and to enter the stratosphere. Here an important natural reaction cycle exists preventing UV radiation from reaching the earth's surface, the so-called Chapman mechanism. This reaction is based on the formation of ozone in higher altitudes by radiation-induced cleavage and rearrangement of oxygen molecules. The formed ozone acts in altitudes around 50 km as UV absorber by photolysis. The continuous synthesis and degradation of ozone lead to an average ozone concentration with a maximum at the stratosphere, the so-called ozone layer.

Also CFC underlie photolysis as their major natural reaction pathway of degradation. Here, the radicals, accordingly formed in the stratosphere, exhibit a significant stability to interfere in the Chapman mechanism. They act as catalysts and accelerate the degradation reaction leading to a significant depletion of ozone in the ozone layer. A schematic description is given in Fig. 2.6. Noteworthy, the ban or strict reduction of CFC initiated by the Montreal Protocol in 1986 led to a significant recovery of the ozone layer.

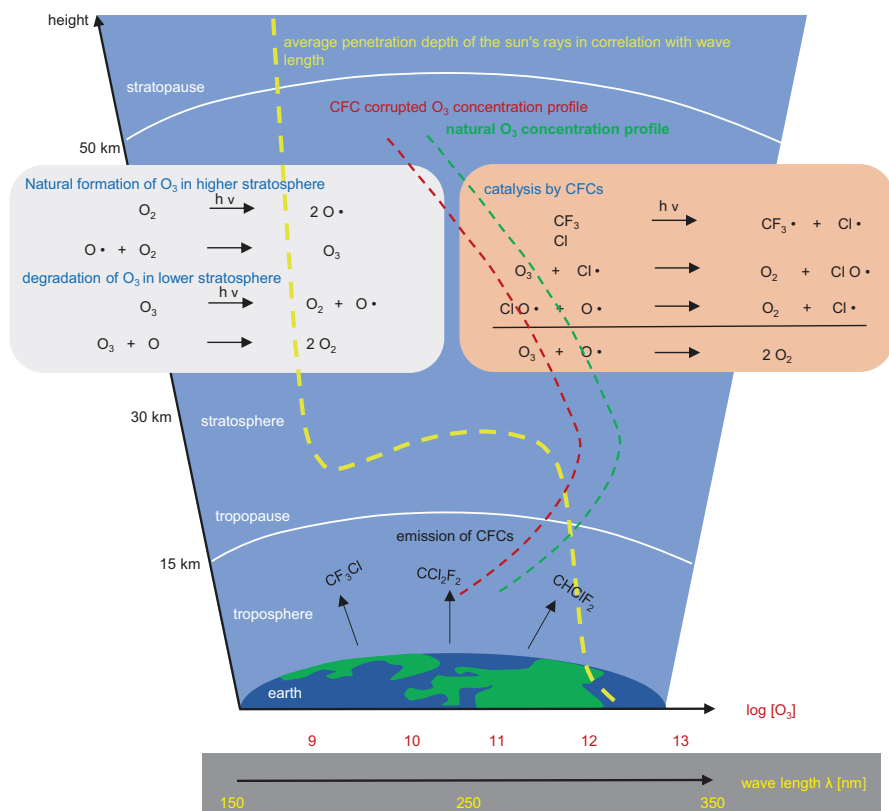
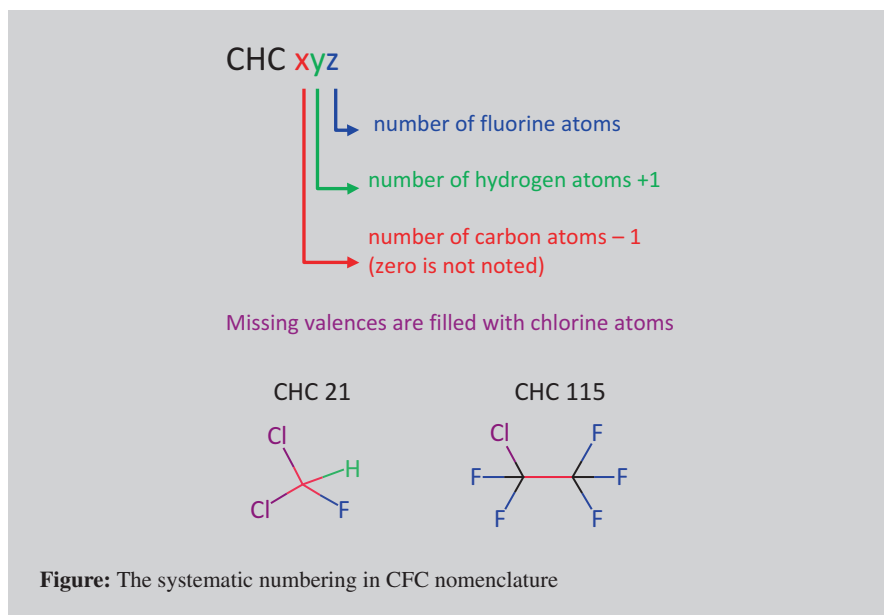


Fig. 2.6 Principal Chapman mechanism forming the ozone layer and the negative influence by CFC

Excursus – A special nomenclature of CFC

Technical CFC products exhibit a special type of designation. Depending on the manufacturer or system a short abbreviation (e.g. Freon, Halon, R-, FCKW, CFC ...) is followed by a systematically produced number reflecting the chemical composition. Three numerals give information about the number of carbon atoms (first numeral: number of carbon atoms minus 1, zero is omitted), of hydrogen atoms (second numeral: number of hydrogen plus 1) and of fluorine atoms (last number). Missing atoms are filled with chlorine atoms. An example is illustrated below.

(continued)



2.1.1.2 PER

Structural similar to CFC, tetrachlorinated ethylene or **per**chlorinated ethene, also named PER, has been used intensively as active agent in dry-cleaning resulting in high production rates on the level of one million tons per year. The lipophilic properties as well as the inflammability made this compound a highly appropriate solvent not only for dry-cleaning of clothing but also in technical applications such as degreasing of metal surfaces. The toxicity of PER is relatively low but PER is classified as probable carcinogenic and can harm the nervous systems.

In the past, careless use and uncontrolled discharge of PER and PER containing waste led to numerous contaminations especially in the pedosphere. Here, the high density of PER induced an emission pathway starting with seeping through the soil zone as a plume. Due to its low boiling point, parts of the contamination can be volatilized, but a major proportion can reach the groundwater systems. Due to its higher density as compared to water, the PER residues form a separate phase sinking slowly down. Therefore, PER is also characterized as so-called dense non-aqueous phase liquid or DNAPL (see Fig. 2.7).

This environmental pathway is accompanied by transformation and degradation process in both the aerobic soil zones as well as the saturated and anaerobic groundwater regions (see Fig. 2.8). Under aerobic conditions a relatively fast dechlorination appears with an epoxidation of the double bond as a central transformation step. Unfortunately, this reaction pathway starts with the first metabolite trichloroethylene, whereas the parent compound PER does not underlie a significant degradation under aerobic conditions. This perchlorinated compound is degradable

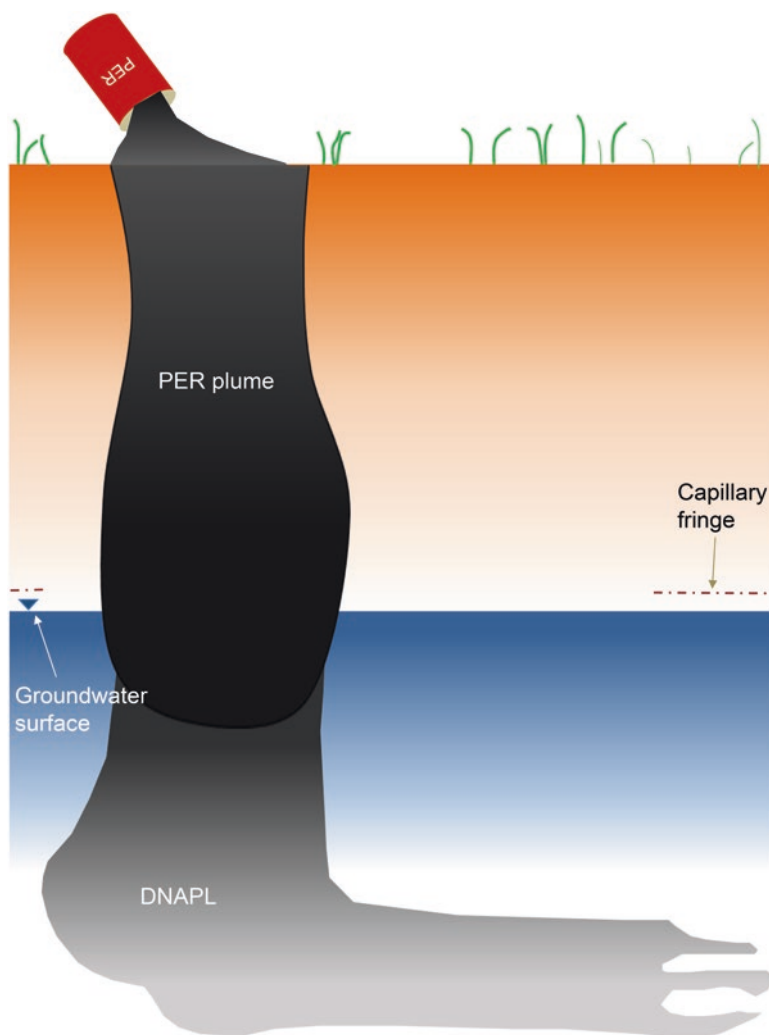


Fig. 2.7 Emission pathway of PER contamination in a soil-groundwater system

mainly under anaerobic conditions by a stepwise reductive dechlorination forming tri- and dichloroethylenes, vinylchloride and finally ethene. However, this degradation pathway is much slower. This complex and partly inverse degradation pathway causes a relative high environmental stability of PER residues in soils and aquifers.

Noteworthy, the toxicological relevance of PER contaminations changes with ongoing anaerobic degradation. As already illustrated in Fig. 1.24 the metabolites exhibit partly higher toxicities and, consequently, degradation of PER does not imply an immediate reduction of environmental risk.

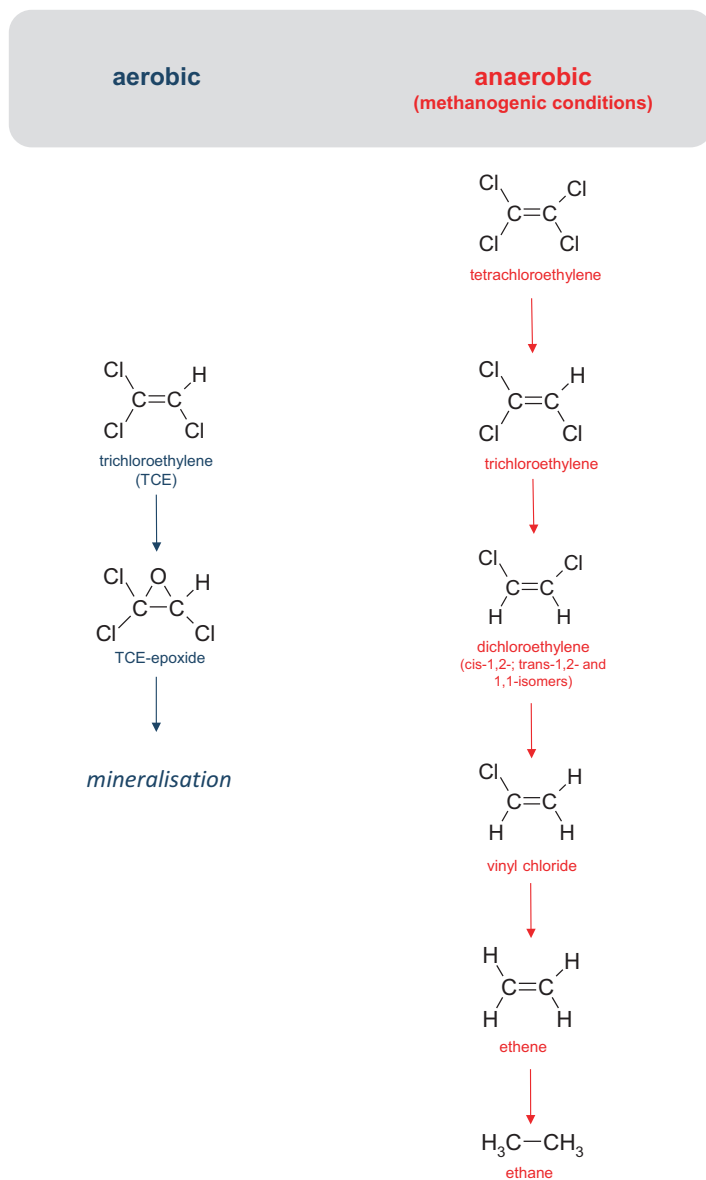


Fig. 2.8 Parallel degradation pathways of PER under aerobic and anaerobic conditions (Modified after Fritsche 1998)

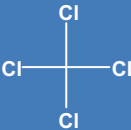
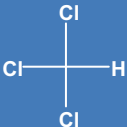

	tetrachloromethane	trichloromethane (chloroform)	dichloromethane
			
boiling point	76.5 °C	62 °C	40 °C
water solubility (25 °C)	793 mg/L	7950 mg/L	13000 mg/L

Fig. 2.9 Chlorinated methanes and some physico-chemical properties with environmental relevance

2.1.1.3 Further Halogenated Aliphatics

Many solvents used in chemical synthesis but also in commercial products are halogenated substances with low molecular weight. Most important solvents are chlorinated methanes, in detail tetrachloro-, tri- and dichloromethane. Varying toxicological properties are known, e.g. hepatotoxicity for CCl_4 . However, trichloromethane, also named chloroform, is a very well-known anesthetic. These representatives are depicted in Fig. 2.9. Systematic changes in physico-chemical properties with increasing number of chlorine atoms are obvious (increasing boiling point but decreasing water solubility).

Chlorinated long chain alkanes from C_{10} to C_{30} with chlorine content of up to 70% are known for decades as industrial compounds used e.g. as plasticizers, lubricants and adhesives. Due to their environmental stability they have been detected in particular in the marine environment. Here a high bioaccumulation potential led to concentrations in the range of 0.1 to 2 $\mu\text{g/g}$ in fishes and mussels (e.g. Tomy et al. 2000).

2.1.2 Halogenated Aromatics

2.1.2.1 Dioxins

The term dioxins summarized a complex mixture of halogenated compounds with two different basic structures: dibenzo-*p*-dioxin and dibenzofuran. Accordingly, dioxins are more accurately named as polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) or in summary PCDD/Fs. Both basic structures exhibit 8 positions at which hydrogen atoms can be substituted by chlorine atoms (see. Fig. 2.10). Variation of number of chlorine atoms (level of chlorination) as well as substitution position (substitution isomers) form the huge group of

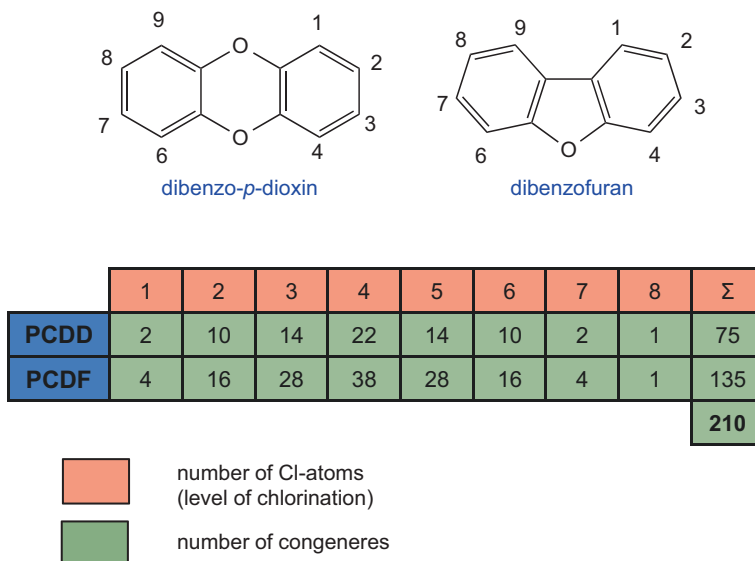
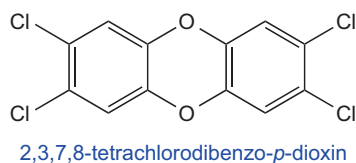


Fig. 2.10 Basic molecular structures of PCDD and PCDFs and their congener multiplicity

Fig. 2.11 The best-known dioxin congener 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), also known as ‘Seveso’ dioxin



congeners. In total 209 congeners exist. A mixed halogenation with chlorine and bromine leads to a total sum of 1700 (PXDD) and 3320 (PXFD) congeners. However, from an environmental point of view only chlorinated dioxins are summarized by the term *dioxins*.

With the term dioxin sometimes only one congener is mentioned, the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin also called ‘Seveso’ dioxin (see Fig. 2.11). This isomer is often used as representative congener, the reasons are discussed later.

Since dioxins cover a complex mixture of congeners also the environmental relevant physico-chemical properties are broader. This is depicted in Fig. 2.12 for the both partitions coefficients K_H and K_{OW} . A systematic shift to higher values is visible for increasing levels of chlorination. Hence, the lipophilicity increases with number of chlorine atoms, whereas the volatility decreases. However, for all congeners a dominant tendency for geo- and bioaccumulation due to a relative high lipophilicity and a low volatility can be stated in general.

Dioxins do not appear in the environment as the result of anthropogenic production and usage. They are emitted unintentionally by various anthropogenic activities. In principal, three different sources can be distinguished: pyrolytic processes, metallurgical processes and formation as byproducts of technical synthesis. Incomplete

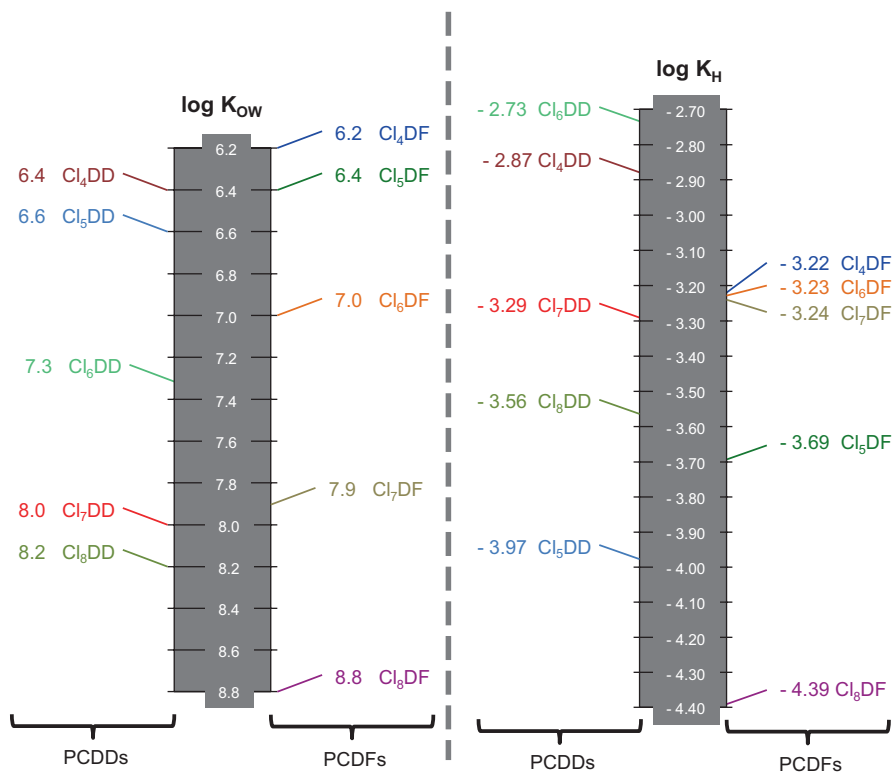


Fig. 2.12 Systematic trends of K_{OW} and K_H values with degree of chlorination of dioxins

combustion or pyrolysis of organic matter can form highly reactive intermediates (radicals, ions) with dominantly two and four carbons and a high degree of unsaturation (e.g. butadiene, ethine ...). These species can easily form aromatic ring systems (see also Sect. 2.7). If chlorine atoms are present during these incomplete combustions, chlorinated aromatics are formed comprising dioxins (see Fig. 2.13). Pyrolytic dioxins can be also formed naturally e.g. by volcanic eruptions or forest fires. However, currently the most dominant sources of pyrolytic dioxins are manmade e.g. emissions from waste incineration or combustion engines (car traffic).

A second source is related to metallurgical processes at high temperatures during which also dioxins are formed unintendedly and are discharged via exhaust, sewage or production waste dumping. As a third origin for dioxins chemical processes are known with synthesis products structurally related to dioxins. During the synthesis of such chlorinated aromatic substances dioxins are often produced unintendedly. Some emission sources and quantitative estimations are given in Fig. 2.14.

This third source became evident by two serious dioxin contaminations. In 1986 an explosion in a chemical plant at Seveso (Italy) released a huge proportion of dioxins. This catastrophe is known as Seveso accident and marked the starting point of an elevated public attention on dioxin pollution. In the course of the accident,

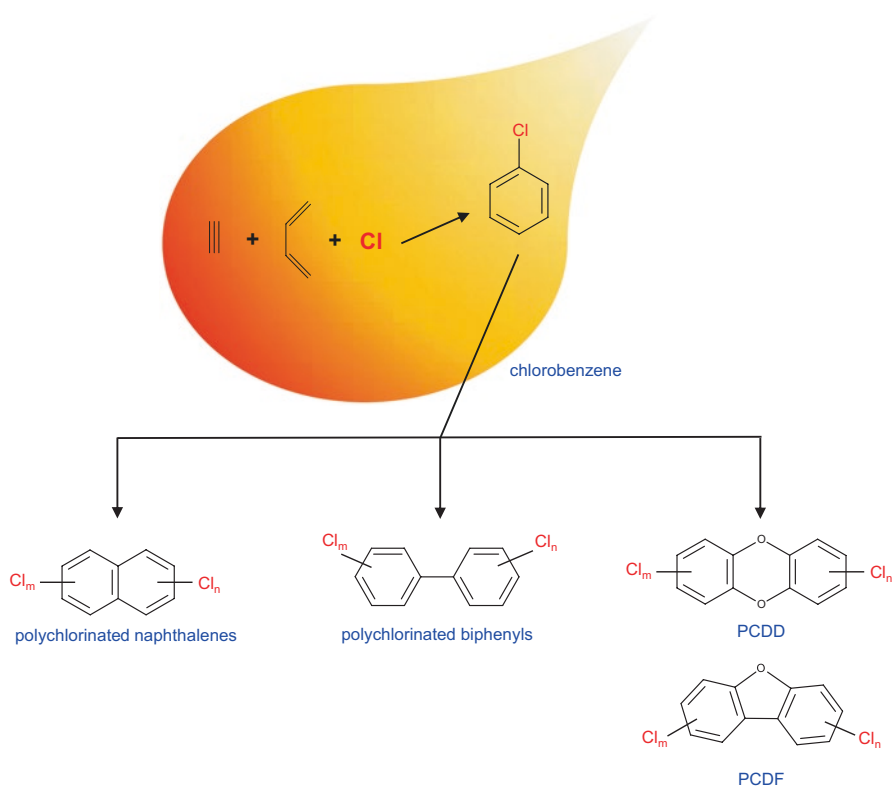


Fig. 2.13 Principal formation pathway of chlorinated aromatics including dioxins during incomplete combustion of organic matter (see also Fig. 2.70)

dominantly one dioxin congener has been emitted, the already introduced ‘Seveso’ dioxin 2,3,7,8-TCDD. The reason for the more or less exclusive formation of this congener is related to the chemical synthesis that became out of control (see Fig. 2.15). The chemical plant produced the herbicide 2,4,5-T, a chlorophenoxyacetic acid. The reaction started with 1,2,4,5-tetrachlorobenzene which was converted in a first step to 2,4,5-trichlorophenol by a substitution reaction with sodium hydroxide under pressure and temperature around 150 °C. The phenol can be coupled easily in a second reaction step with chloroacetic acid to receive the final product. However, the first reaction is the critical step since at slightly higher temperature (as during the explosion) above 180 °C a competitive condensation and cyclisation can form the 2,3,7,8-TCDD. Hence, the structural properties of the educt 1,2,4,5-tetrachlorobenzene defined the resulting dioxin congener.

This side reaction occurs not only during accidents but also to a very limited extent during the normal synthesis of 2,4,5-T. However, this very low amounts of byproducts exhibit a high relevance since the main product, a herbicide, is directly emitted to the environment. These impurities have led to an enormous contamination

				PCDD/PCDF [g TEQ/a]
pyrogenic sources	MVA fly ash	FRG	1990	3000
	road transport			111
	fossil fuels - domestic use	Australia	1998	2.5
metallurgy	metallurgical processes	FRG	1990	3500
	non-ferrous metals			136
	aluminium production	Australia	1998	32
byproducts	usage of PCP	Netherlands	1990	460
	wood preservation			381
	pulp and paper production	Australia	1998	110
		products	application	
for example:		pentachlorophenol, PCP	fungicide	
		hexachlorophene	bactericide	
		polychlorinated biphenyls, PCBs	technical additive	

Fig. 2.14 Principal emission sources of dioxins (see also Ballschmitter and Bacher 1996)

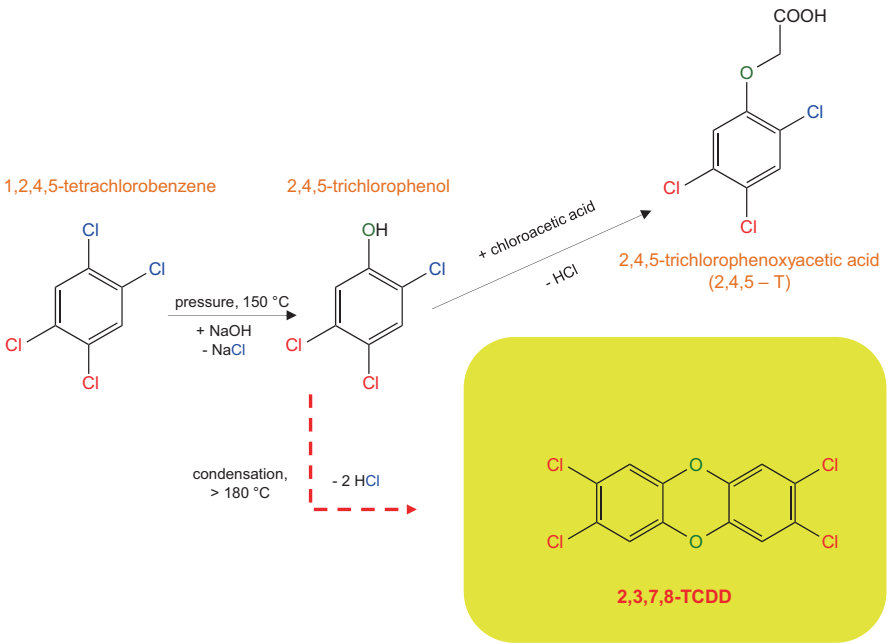


Fig. 2.15 Formation of 2,3,7,8-TCDD during the Seveso accident (Modified after Voß 1997)

during the Vietnam war. The US air force sprayed more than 50.000.000 liters of 2,4,5-T and 2,4-D (named *Agent Orange*) as defoliant and contemporary more than 150 kg of dioxin impurities dominantly consisting of 2,3,7,8-TCDD. The reason for the dominant appearance of this congener is discussed above. Several millions of people were exposed and suffer till now from this intoxication.

Many more diffuse emissions of dioxins are not dominated by one isomer as explained for the Seveso disaster as well as the technical synthesis of Agent Orange. In particular, pyrogenic sources discharge dioxin mixtures of more complexity but also of more specificity. In Fig. 2.16 some dioxin pattern with respect to the individual levels of chlorination for both furans and dioxins are depicted. Clear differences in

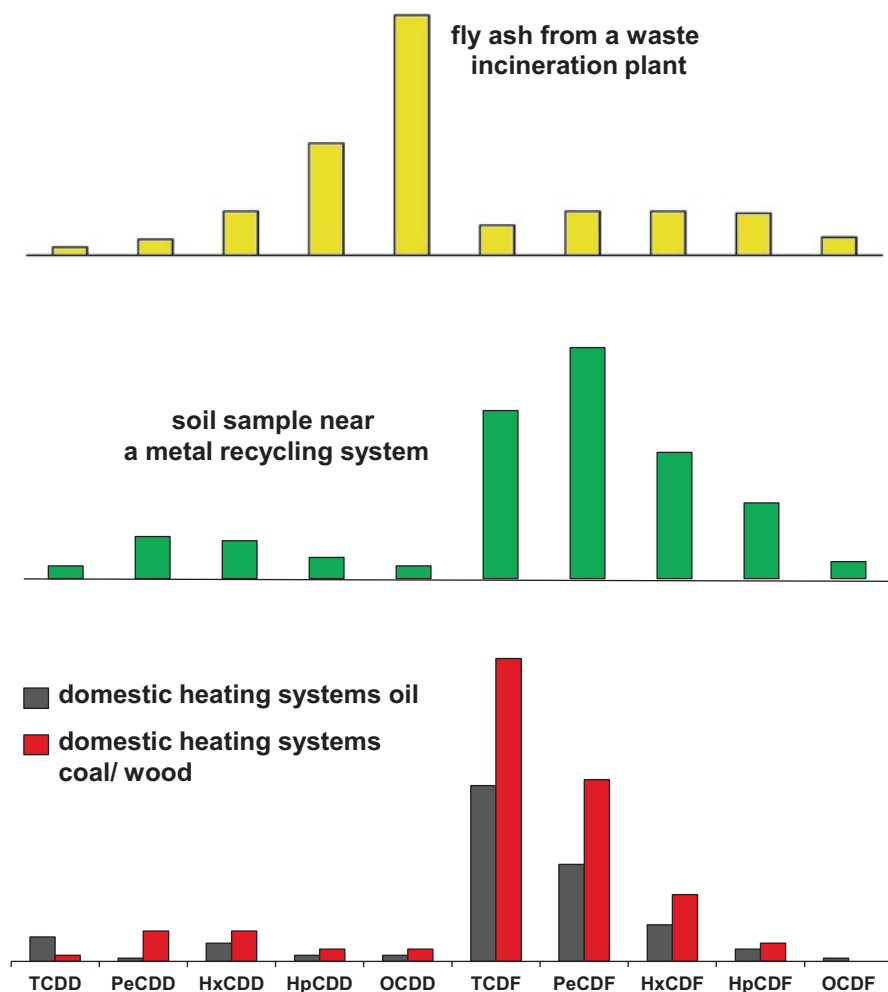


Fig. 2.16 Different dioxin pattern according to the level of chlorination for PCDDFs from different emission sources (Adapted from Ballschmitter and Bacher 1996)

relative compositions for the different pyrogenic emission sources are obvious and can be used *vice versa* for source apportionment of dioxin pollution in environmental samples. Principally, such ‘finger printing’ is only possible for complex mixture produced for example by congeners.

As a further aspect of the environmental impact of dioxins, their toxicity is reported in a very specific way. The system of *Toxic Equivalence* (TEQ) has been introduced to simplify the delineation of the risk potential of dioxin contamination (see Fig. 2.17). Principally, it is a normalization and reflection on the most toxic congener, the 2,3,7,8-TCDD. Instead of the total sum of the amounts of all congeners, a *Toxic Equivalent Factor* (TEF) is attributed to all individual congeners. These factors represent the relative toxicity in comparison to 2,3,7,8-TCDD. Since this congener is the most toxic one, all factors range between 0 and 1. As an example, a TEF value of 0.1 reflects a toxicity of 10% for the corresponding congener. To calculate the total TEQ the concentrations of all congeners are multiplied with the TEF and are summed up. This value given for example as ‘ng TE/g’ is lower as compared to the total amount of all dioxin congeners but reflects the total toxicity of the dioxin contamination. In other words, the TEQ values represent the toxicity corresponding to a contamination solely by 2,3,7,8-TCDD on the TEQ concentration level.

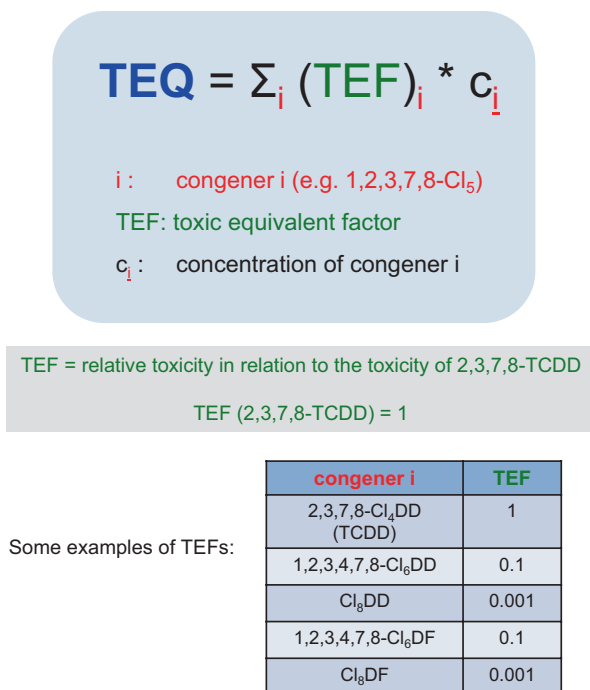


Fig. 2.17 The system of *Toxicity Equivalence*

congener	US (EPA)	Nordic system	Germany (BGA)	NATO	WHO
2,3,7,8-Cl ₄ DD (TCDD)	1	1	1	1	1
1,2,3,7,8-Cl ₅ DD	0.5	0.5	0.1	0.5	1
1,2,3,4,6,7,8-Cl ₆ DD	0	0.001	0.001	0.001	0.0001
2,3,7,8-Cl ₄ DF	0.1	0.1	0.1	0.1	0.1
1,2,3,7,8-Cl ₅ DF	0.1	0.01	0.1	0.05	0.05
2,3,4,7,8-Cl ₅ DF	0.1	0.5	0.1	0.5	0.5
1,2,3,4,7,8,9-Cl ₆ DF	0	0.001	0.001	0.001	0.0001

national systems
international systems

Fig. 2.18 Extracted TEF values from different systems. Note the differences in TEF values

Table 2.2 Some toxicological parameters for dioxin

	LD ₅₀ of TCDD [μg/kg]	Teratogenic effects [μg/kg]	ADI [pg TEQ/kg bodyweight]			estimated intake [pg TEQ/kg bodyweight]
			WHO	Germany	USA	
Cavy	0.5–2.0					
Rat	22–60	0.5				
Mouse	114–284	1–3				
Human (adult)			1–4	10	0.006	Germany: 2

ADI acceptable daily intake

LD₅₀: median lethal dose (dose, at which 50% of the exposed animals die)

Noteworthy, various TEF systems exist with slight differences in the toxicity assessment of individual congeners. For example, the TEF of important systems are exemplified in Fig. 2.18. Nowadays the international systems are the commonly used ones.

Beside this toxicity systems also further parameter characterize the risk of dioxin contaminations. Acute toxicity values from tests on animals or recommendations for precautions like the *acceptable daily intake* ADI are measured or calculated. Some exemplifying values are given in Table 2.2.

2.1.2.2 PCBs

A similar publicity as compared to dioxins hold also the group of polychlorinated biphenyls, the PCBs. They form a group of congeners, in which the basic structure of biphenyl can be substituted by up to 10 chlorine atoms at different positions forming 209 possible congeners. A systematic nomenclature as described in Fig. 2.19 has been complemented by K. Ballschmiter just numbering all congeners.

Excursus – Commercial PCB products

PCB mixtures are commercially available with different compositions regarding their chlorine content or degree of chlorination. Most of the commercial names consist of a short name and a following number containing information on the chlorine content. This is exemplified below for *Aroclor* and *Chlophen*, products from the companies Monsanto and Bayer, respectively.

Commercial products

Aroclor 1242: 1 % Cl₁-CB + 13 % Cl₂-CB + 45 % Cl₃-CB + 31 % Cl₄-CB + 10 % Cl₅-CB

total chlorine content **42%**

Chlophen A60: 1 % Cl₄-CB + 13 % Cl₅-CB + 51 % Cl₆-CB + 30 % Cl₇-CB + 4 % Cl₈-CB + <1 % Cl₉-CB

total chlorine content **59%**

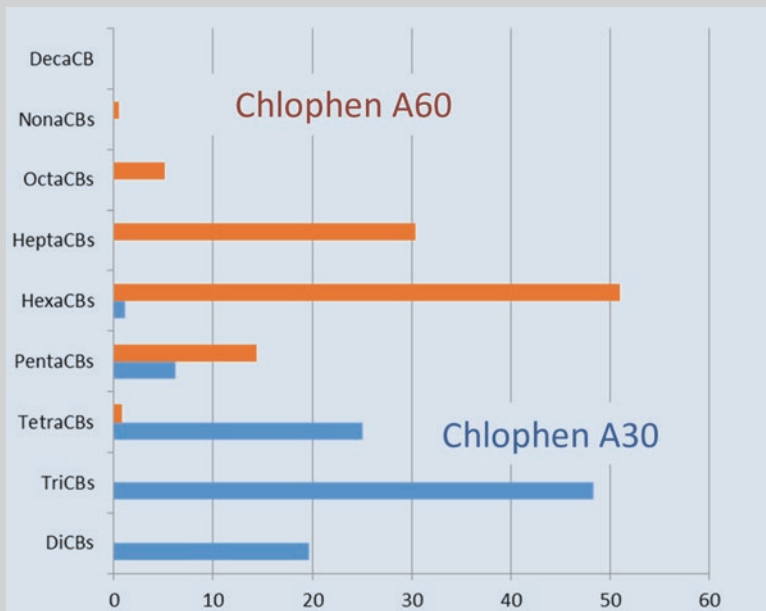


Figure: Two examples of commercial names and the composition behind the names. Differences between technical formulations from one producer are illustrated by the composition of Chlophen A30 and A60 (According to Schulz et al. 1989)

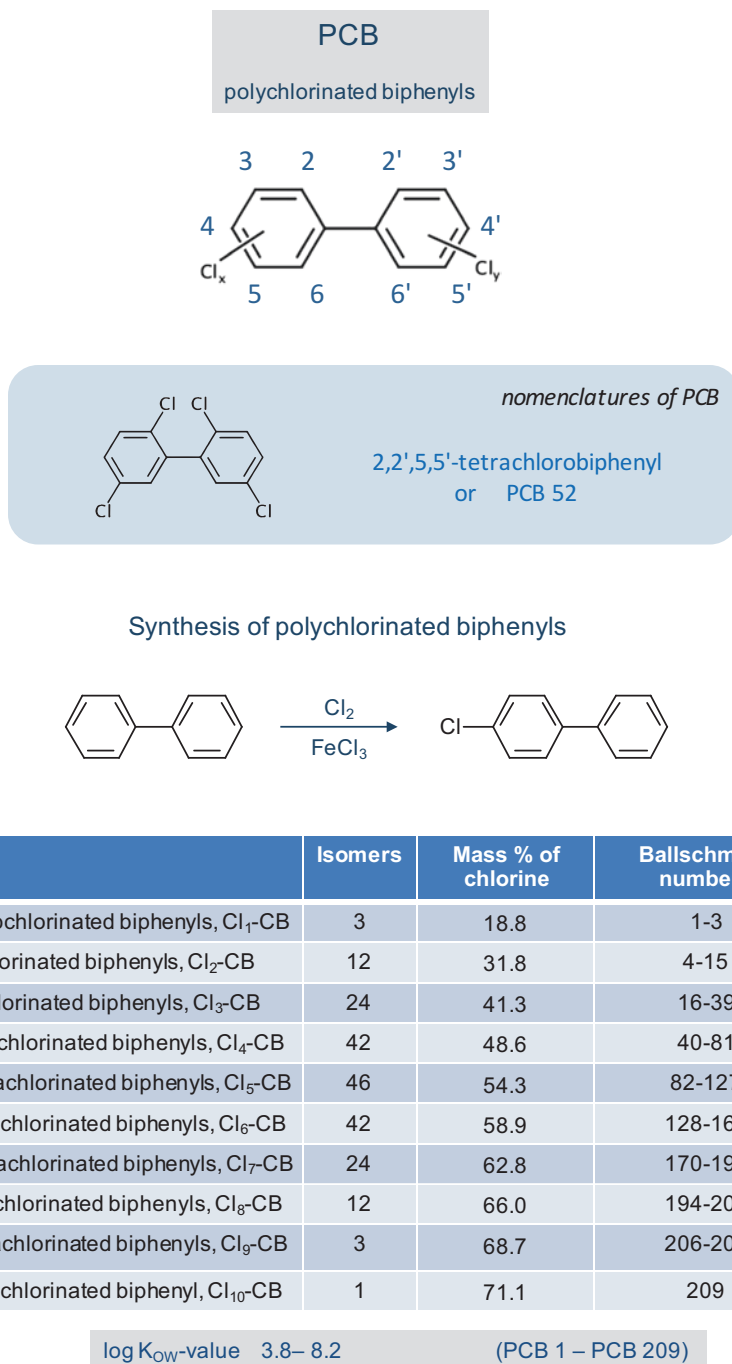


Fig. 2.19 Structural properties, nomenclature and list of congener groups of PCBs

The environmental properties of PCB cover a high persistence. They also belong to the *Dirty Dozen* banned by the *Stockholm Convention* in 2004 (see Chap. 4). Depending on the degree of chlorination they are relatively stable against biotic degradation but also against abiotic attacks e.g. by strong acids, light or temperature. They exhibit a very low flammability.

In 1876 PCBs were synthesized for the first time but commercial synthesis started in 1929 by reaction of biphenyl with chlorine using a catalyst. The amount of chlorine gas used determines the average degree of chlorination. Technical products cover a wider range of chlorine content or degree of chlorination. Since the chlorine content is responsible for variation in physico-chemical characteristics (e.g. viscosity) the different products have been synthesized for different fields of application. Low molecular weight products have been used as constituents of hydraulic fluids e.g. in the mining industry. Higher chlorinated mixtures have been added e.g. to transformer oils. Noteworthy, two different modes of application have to be differentiated, the open and closed applications. Open applications (e.g. usage as plasticizers) spreading PCBs uncontrolled to the environment have been forbidden already in the 1970s in many industrialized countries. The usage in closed systems (e.g. as insulator oils) has been partly restricted years later.

From an analytical point of view PCBs exhibit very specific congeneric profiles. As already mentioned, the proportion of fractions with the same number of chlorines differ in technical mixtures. But due to the simple and widely uniform synthesis, the patterns of substitution isomers within one degree of chlorination do not vary significantly (see Fig. 2.20). These patterns can be used to identify technical PCB contamination but more important these uniform profiles lead to an analytical reduction. Instead of analyzing all congeners only one (or at least two) isomers per degree of chlorination are measured as representatives. For quantifying the total PCB contamination the sum of all representative PCBs is just multiplied by a constant value (around 5) that reflects their constant relative proportion. Such leading PCB congeners are for example PCB 28 ($\text{Cl}_3\text{-PCB}$), PCB 52 ($\text{Cl}_4\text{-PCB}$), PCB 101 ($\text{Cl}_5\text{-PCB}$), PCB 153 ($\text{Cl}_6\text{-PCB}$) or PCB 180 ($\text{Cl}_7\text{-PCB}$).

Since their first environmental detection in the 1960s, PCBs are detectable ubiquitous till now. Due to their lipophilicity (see K_{OW} value in Fig. 2.19) and low vapor pressure, they tend to accumulate in soils and sediments as well as biota. Some exemplifying data for one ecosystem are summarized in Table 2.3.

The environmental stability of PCBs is high but these compounds are certainly also subject to degradation. Under aerobic conditions the hydroxylation of the aromatic ring is the dominant pathway. Main parameter for the degradation rate is the level and position of chlorination. Lower chlorinated PCBs can be degraded faster and the substitution pattern directs the attack by oxygenase. As a competitive transformation for selected congeners also the formation of methylthio and after oxidation of methylsulfone substituted metabolites have been observed (see Fig. 2.21). In marine mammals and sea birds, concentrations of these metabolites have been determined at a level of 0.01–10 $\mu\text{g/g}$.

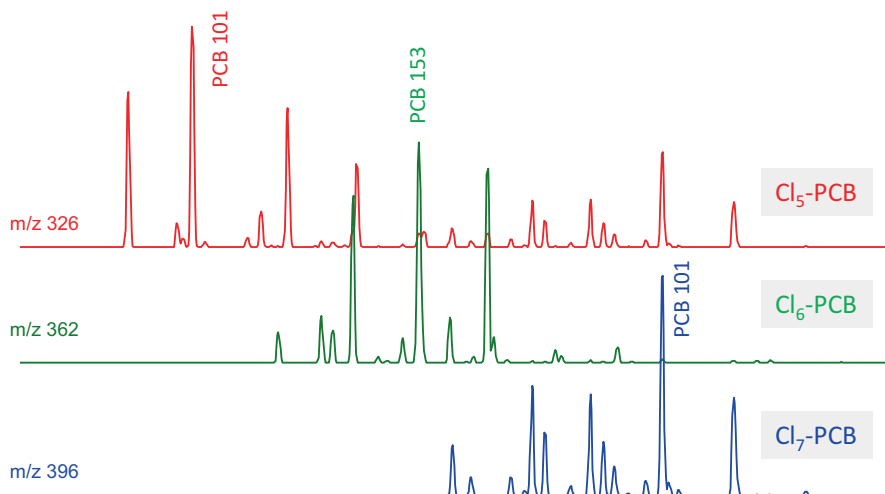


Fig. 2.20 Ion chromatograms of individual isomer profiles of PCB with different degree of chlorination

Table 2.3 Selected environmental data of PCB in an aquatic ecosystem

Sample	Σ PCB-concentration
Water	0.5–12.5 ng/L
Sediment	4.2–4600 ng/g
Catfish tissue (several types)	4–1600 ng/g
Crab tissue (<i>Calinectes sapidus</i>)	3.4–170 ng/g

Data from Howell et al. (2008)

The toxicity of PCBs has been evaluated in many tests and relatively low acute toxicities have been reported (e.g. LD₅₀ values for rodents around 1–9 g/kg body weight). Test results for chronic toxicities were certainly lower and range e.g. between 0.1 and 1 mg/(kg*day) for monkeys. However, acute and in particular chronic toxic effects for humans have been monitored in detail during PCB accidents. In 1968 several thousand people in Japan have been poisoned by PCB contaminated rice. The observed effects (also the long lasting) have been summarized as *Yusho* disease. In 1978 a similar accident (here a PCB contamination of rice oil) led 1978 to a mass poisoning in Taiwan, the symptoms have been named *Yu Sheng* disease.

PCBs can induce different types of toxicity. This depends *inter alia* on the substitution pattern, in particular at the *ortho* position. Biphenyl molecules can rotate around the linkage between the phenyl moieties. The aromatic rings can be orientated in a plain conformation or with a 90° rotation. This is valid also for PCBs with chlorine substitution at *meta* or *para* position. This degree of freedom is hindered by substituents at *ortho* position due to steric hindrance (see Fig. 2.22). For the toxicity both conformations exhibit different possibilities to interact with biological receptors in organism leading to different toxicities. The non-*ortho*-substituted PCBs,

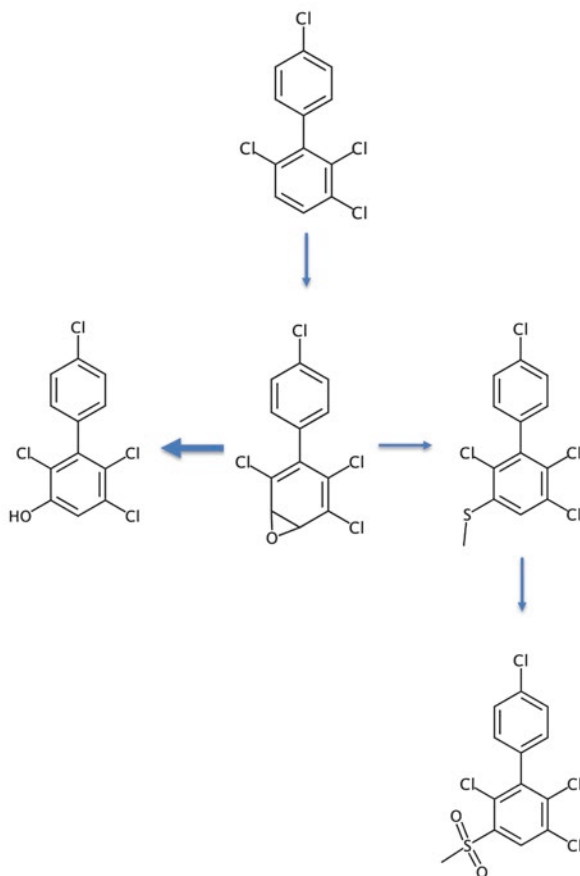


Fig. 2.21 Formation of PCB metabolites under aerobic conditions. Beside the main transformation forming hydroxyl metabolites also thioether groups are formed. The formation of the methylthio-/methylsulfone metabolites depends on the chlorine substitution pattern and is preferred by 3,4-non-substituted isomers

also called coplanar PBS, have a plain structure and a chlorination pattern similar to the more toxic dioxins, hence their toxicological effects are alike. These congeners (e.g. 3,4,4',5-tetrachlorobiphenyl or PCB 81) are also called **dioxin-like PCB** or **dl-PCB**. Accordingly, for coplanar PCBs also TEF have been determined reflecting the contribution of these PCB isomers to the dioxin-like effects in environmental samples (see Table 2.4).

The ban of PCB has partly led to substitution by other, chemically similar, products. As an example, in the German mining industry isomer mixtures of tetrachlorinated benzyltoluenes (TCBT, see Fig. 2.23) have been introduced as PCB-substituents in the mid 1970s. Due to the high structural similarity, it is not surprising that the technical formulations, also called Ugilec 141, exhibit comparable properties with respect to environmental stability and accumulation. Therefore, TCBTs

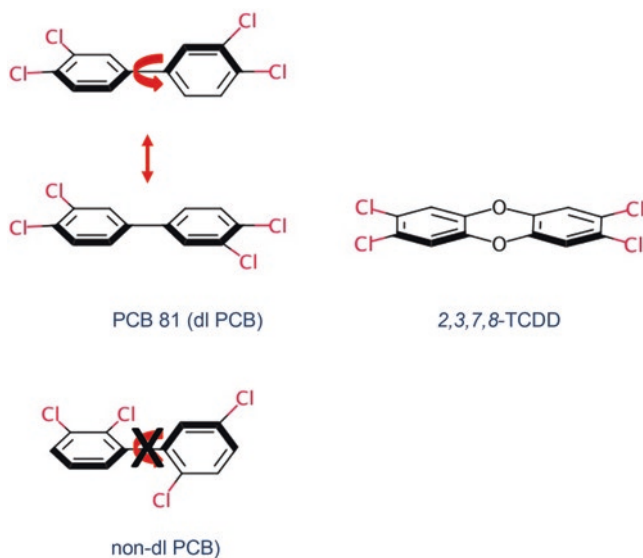


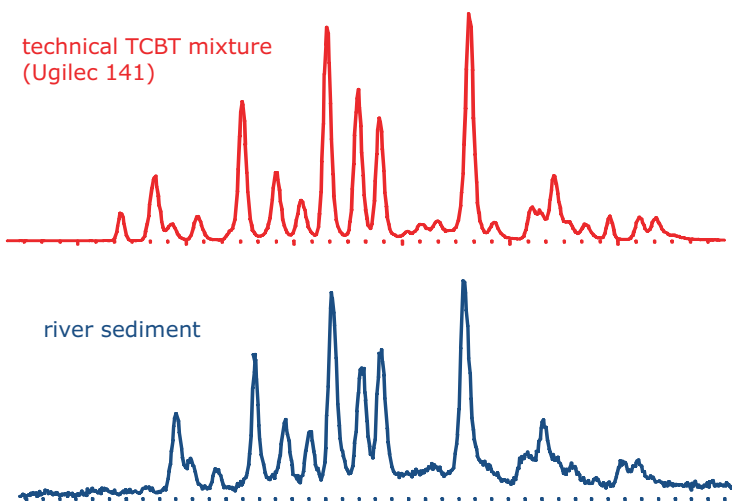
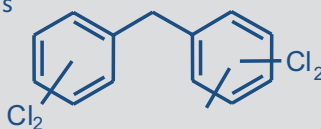
Fig. 2.22 Rotation in PCB molecules is hindered by 2-substitutions but for so-called dl-PCB the rotation allows a configuration forming a planar structure similar to dioxins. This explains the dioxin like toxicity of these specific PCB congeners

Table 2.4 Toxic equivalent factors TEF for dl-PCBs (According to WHO)

PCB		TEF
PCB 77	3,3',4,4'-Tetrachlorobiphenyl	0.0001
PCB 81	3,4,4',5-Tetrachlorobiphenyl	0.0001
PCB 126	3,3',4,4',5-Pentachlorobiphenyl	0.1
PCB 169	3,3',4,4',5,5'-Hexachlorobiphenyl	0.01
PCB 105	2,3,3',4,4'-Pentachlorobiphenyl	0.0001
PCB 114	2,3,4,4',5-Pentachlorobiphenyl	0.0005
PCB 118	2,3',4,4',5-Pentachlorobiphenyl	0.0001
PCB 157	2,3,3',4,4',5'-Hexachlorobiphenyl	0.0005
PCB 167	2,3',4,4',5,5'-Hexachlorobiphenyl	0.00001
PCB 189	2,3,3',4,4',5,5'-Heptachlorobiphenyl	0,001

have been detected in Germany in the same environmental systems as mining derived PCBs. Some exemplifying data are presented in Fig. 2.23. Noteworthy, also similar to PCBs the gas chromatographic pattern of technical TCBT mixture exhibits a high specificity and can be used for an unambiguous source apportionment of contamination measured in natural samples (see Fig. 2.23).

Tetrachlorobenzyltoluenes - TCBTs

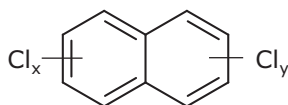


River	Sample	Concentrations (ng/g)	Reference
Rur	Sediments	85 - 2685	Poppe et al. 1991
	Fish	<20 - 24900	Fürst et al. 1987
Saar	Sediments	<10 - 12850	Breitung 1992
Lippe	Sediments	<10 - 2400	Kronimus et al. 2004
	Fish	100 - 4700	Poppe et al. 1988

Fig. 2.23 Molecular structure of TCBTs, their highly source specific gas chromatographic pattern (Adapted from Kronimus et al. 2004) as well as some environmental data measured in German rivers affected by mining activities

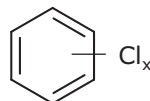
2.1.2.3 Further Halogenated Aromatics

Besides PCBs and PCDD/Fs many other halogenated aromatic compounds are known, partly just as byproducts e.g. by technical synthesis (e.g. mixtures of chlorinated di- and triphenylmethanes) or pyrolysis processes but dominantly produced as technical agents. Some examples are given in Fig. 2.24.



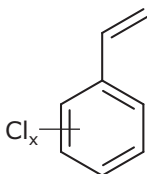
polychlorinated naphthalenes
PCN

Herring (Baltic Sea): 2-26 ng/g
Fly ash (Stockholm, Sweden): 28 ng/g
Sediment (Eman river, Sweden): 2- 270 ng/g



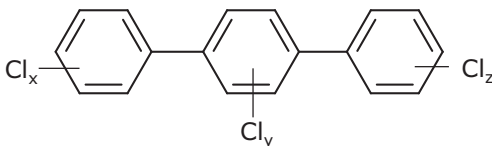
polychlorinated benzenes
PCBz

Cod liver (North Sea): 400 ng/g
Soils Germany): up to 8000 ng/g



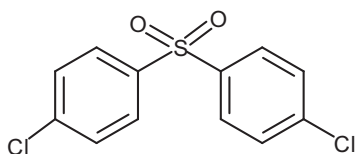
polychlorinated styrenes
PCS

Fish (North Atlantic): 1-88 ng/g fat
Sediments (Teltow Canal, Berlin): 100-800 ng/g



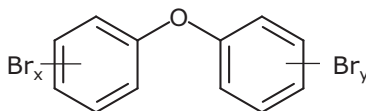
polychlorinated terphenyls
PCT

Cod liver (North Sea): 410 ng/g
Sediments (Rhine river, Germany): 80 ng/g



bis(4-chlorophenyl)sulfone
BCPS

Blubber of Grey Seal (Norway): 50-90 ng/g
Sediments (Mulde river, Germany): 110 – 200 ng/g



(poly)brominated diphenylethers
BDE

Eggs of white-tailed sea eagle (Norway): 800 ng/g
Sediments (Elbe river, Germany): 1 – 20 ng/g

lopamidol
x-ray contrast media

Surface water (Rhine river, Germany): 170 ng/L
Groundwater (Germany): 100 – 1000 ng/L

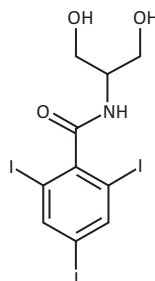


Fig. 2.24 Several halogenated aromatics with environmental relevance (data collected from Heim et al. 2005; Coelhan et al. 2000; Wester and de Boer 1996; Järnberg et al. 1997; Law et al. 2006; Olsson and Bergman 1995; Ternes and Hirsch 2000; Berger and Schwarzbauer 2016)

One emerging group are the polybrominated aromatics such as polybrominated diphenylethers or tetrabromobisphenol A that are frequently used as flame retardants. Further on, many chlorinated aromatics such as polychlorinated styrenes, naphthalenes and terphenyls are technically used and often discharged by both municipal and industrial emissions. A more specific field of application is known for selected iodine substituted aromatics. 1,3,5-Triiodobenzenes further substituted with various polar substituents form the group of x-ray contrast media applied in medical diagnostics. Also for these compounds (e.g. iopamidol, iopromide and iomeprol) an elevated environmental stability has been observed leading to a contamination in particular of the aquatic environment.

General Note

Generally, halogenated aromatics form mixtures of congeners. These mixtures exhibit unique patterns that allow an unambiguous identification of corresponding technical product in natural samples. Further on, the individual congeners exhibit different potential for (eco)toxicological effects but also for biotic degradation. Hence, the number and position of halogen substituents are main parameters for defining the environmental relevance of most of the halogenated aromatics.

2.2 Pesticides

Outlook

Pesticides are chemicals emitted anthropogenically to the environment on purpose. These substances cover a wide range of molecular and physico-chemical properties resulting in very different environment pathways and risks. Beside an overview on pesticide groups a few representatives like DDT are introduced exemplarily in detail.

Keywords Insecticides • Herbicides • Fungicides • DDT • Lindane • Pyrethroids

For millenniums humans have been used pesticides to protect their agricultural crop, to heighten the cultivation efficiency and to avoid any harm by pests. Principally all chemicals used for these purposes are called pesticides. Considering their field of application and the aim of pesticide usage two subgroups can be differentiated. Agents protecting agricultural crops are plant protection products, whereas chemicals controlling organism that are harmful for humans and their products (exclusive agricultural products) are biocides. However, the term ‘biocides’, ‘pesticides’ and ‘plant protection products’ are often confused, especially because many active ingredients are used complementarily in all of these agents.

Table 2.5 A short summary of some benefits and risks related to pesticide usage

Beneficial properties	Negative properties
Protecting harvests and raising yields	Toxic to humans
Protecting milk and meat production	Persistence and global spread
Reducing the risk of losses during food storage	Accumulation in tissues of biota
Prevention of dangerous epidemic plagues	Negative influence on beneficial organisms, soil organisms and soil fertility
Improvement of body hygiene	Difficult in dosage
Reduction in staff (farm workers)	Pollution of ground and surface water
	Effects drinking water
	Disruption of biological sewage treatment plants
	Toxic to crop plants

Modified after Bliefert (2002)

Table 2.6 Principal fields of application of most important pesticide groups

Pesticides	Effective against	Substance class (examples)
Insecticides	Insects	Halogenated hydrocarbons (aldrin, dieldrin, heptachlor, DDT, lindane); pyrethroids; phosphoric acid esters (malathion, parathion, systox); carbamates (pyramid)
Fungicides	Fungi or fungal spores	Different substance classes, often organometallic compounds (with Sn, Zn, Hg)
Herbicides	Weed	Phenoxycarboxylic acids (2,4-D, 2,4,5-T); heterocyclic compounds (atrazine, paraquat)
Acaricides	Mites	Different substance classes
Molluscicides	Snails	Substituted phenols (pentachlorophenol)
Rodenticides	Rodents	Cumarine derivatives (racumin)

Simplified after Heintz and Reinhardt (1991)

Application of pesticides considers a direct and intended emission of these compounds towards the environment. Further on, harmful effects on organism are purposed. In conjunction with the already introduced intention for using pesticides a clear area of conflict becomes evident. Therefore, the usage of pesticides needs a well-reasoned balance of getting benefits and avoiding environmental damages and risks. These both aspects are summarized in more detail in Table 2.5.

Principally, pesticides can be differentiated according to the organisms against which they are utilized. Most important groups in terms of amount used are insecticides, herbicides and fungicides but also more specialized agents exist. Selected representative groups are listed in Table 2.6. The different target organism depict clearly why pesticides are used as both biocides and plant protection products. As an example, measures against mice and rats (rodents) are applied in urban areas for pest control and also for protecting crop.

A further classification of pesticides is based on their chemical properties. This is also related to the different pesticide generations. Very effective pesticides belong to the group of chlorinated hydrocarbons such as DDT or lindane. They have been introduced in the beginning to the mid of the twentieth century. However, these compounds exhibit a high persistence (see also Sect. 2.1) and consequently, a high risk for the environment due to geo- and bioaccumulation tendencies. Therefore, further pesticides have been developed and introduced. These more modern pesticides exhibit a much better degradation potential or lower half-life time that has been achieved by higher functionalized substances, in particular with hydrolysable moieties like ester groups. These pesticides belong e.g. to carbamates, urea derivatives or thiophosphoric acid esters. A principal classification according to the chemical structures is given in Fig. 2.25.

The different chemical and physical properties imply different environmental behavior and need to be considered in the assessment of pesticide application. Different aspects have to be regarded in particular with respect to the soil systems (see Fig. 2.26). Higher functionalized substances are often better water soluble and more bioavailable leading to a faster degradation but also to higher mobility with percolating water towards the groundwater. Hence, for this type of pesticides the low tendency for bio- or geoaccumulation and the fast degradation have to be considered as environmental positive aspects. On the contrary, a risk for groundwater but also adverse economic effects (multiple application per growth period due to a shortened effective time) have to be stated as negative aspects. Looking on the more stable pesticides (e.g. chlorinated hydrocarbons), no mobilization towards groundwater and also just single applications are expected but an elevated risk for geo- and bioaccumulation due to the long half-life times and the lipophilicity have to be considered.

These implications are illustrated by three examples in Fig. 2.27. As a consequence, fine-tuning of chemical and physico-chemical properties is needed to optimize the pesticide usage meeting both economic and environmental interests.

As demonstrated, the environmental behavior of pesticides in soil systems is triggered by two main factors. A first one is the partition behavior between water and the particulate matter, which is specified by water solubility, partition coefficients (like K_{ow} values) and similar parameters. However, molecular properties determine such parameters. As an example, for adsorption on soil particles the acidic/alkaline properties of pesticides are important factors (see Fig. 2.28). Acidic substances tend to be mobilized by leakage water reaching the groundwater systems, whereas alkaline compounds have a strong adsorption potential specially to clay minerals. A similar, strong adsorption potential can be observed for non-ionic and lipophilic compounds but here to the soil organic matter (SOM).

A second main parameter for assessing pesticide risks in soil systems is the environmental stability or even persistence. As already noted, also transformation or degradation potential is closely related to the chemical structure. Therefore, there is a very rough rule of thumb linking chemical class of pesticides with half-life times as presented in Fig. 2.29.

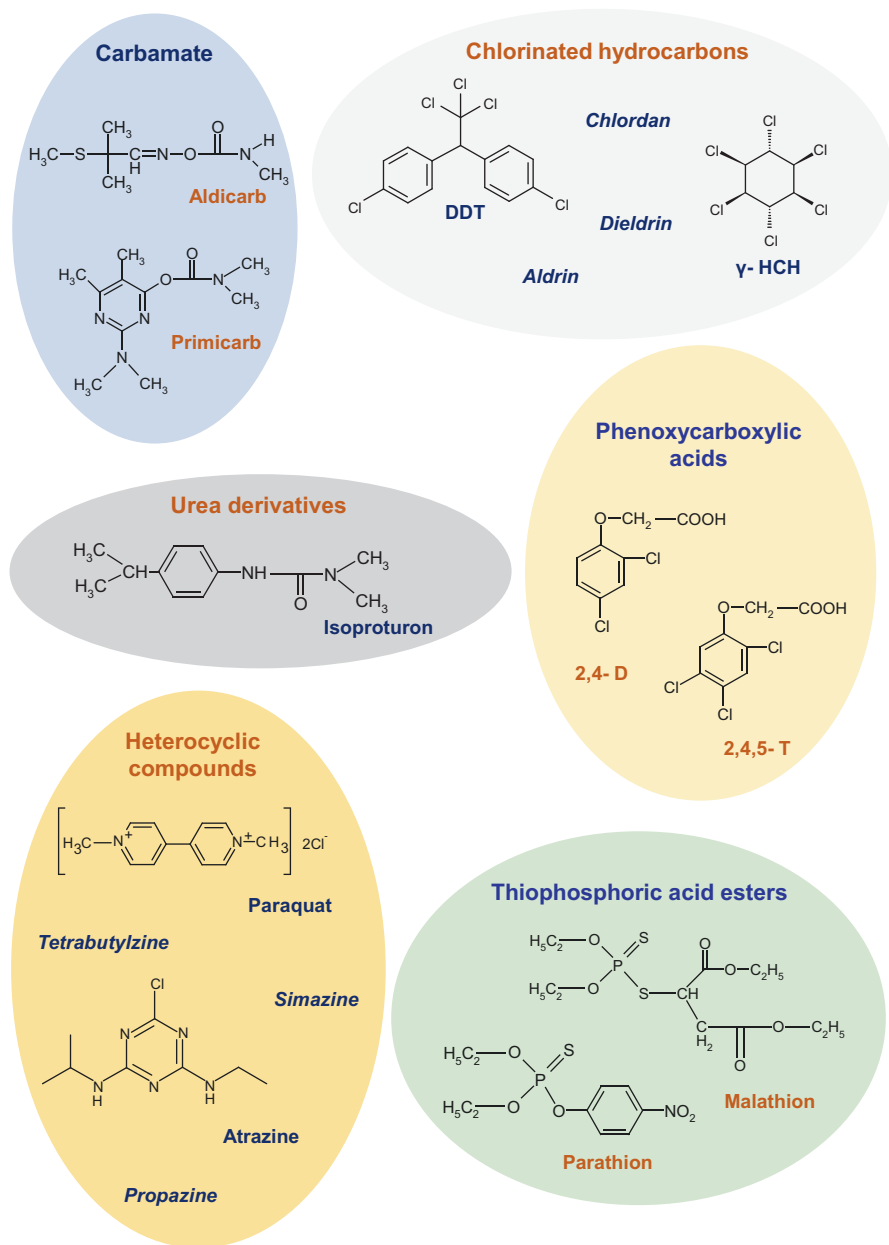


Fig. 2.25 An overview on principal substance classes of pesticides and some representatives (Summarized according to Heintz and Reinhardt 1991 and Bliefert 2002)

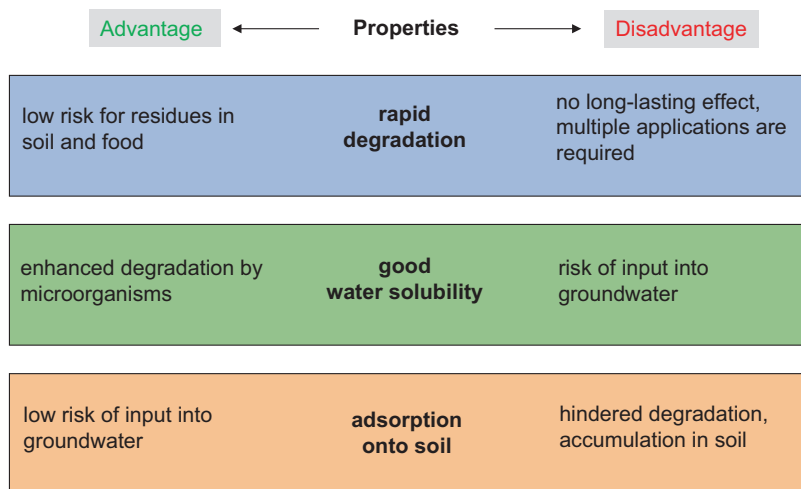


Fig. 2.26 Summary of conflicts in application of pesticides with different physico-chemical properties

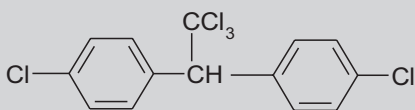
The organic-geochemical relevance of pesticides and the complexity of their environmental occurrence can be described best by the very well-known 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane, also named DDT. DDT has been synthesized first in 1874 but just out of academic interest. In 1939 a screening study for pesticides performed by Paul Hermann Müller revealed DDT as a highly effective agent and from this time DDT started its worldwide dissemination. Firstly, DDT has been used for military purposes but after World War II it has been widely used in agriculture and related fields. In parallel, due to its remarkable efficiency against mosquitoes, DDT has been applied worldwide against malaria disease, partly till now.

In the 1960s the negative effects of DDT and related, highly persistent substances became obvious and DDT has been banned firstly for agricultural application in most of the industrialized countries. In 2004, it has been banned worldwide by the Stockholm Convention (see Chap. 4). The history of DDT, comprising its positive and negative aspects, is summarized in Fig. 2.30.

The ban of DDT is based on its (eco)toxicological effects as well as its high persistence and accumulation potential. From a toxicological point of view, its chronic toxicity including endocrine disrupting effects and probable carcinogenicity have more relevance as compared to the more moderate acute toxicity. The potential to act as endocrine disruptor became clearly obvious by an accident in the US. In 1980 an unintended discharge of DDE (a DDT metabolite) contaminated the lake Apopka (Florida) and had a high impact on its alligator population. Several effects have been observed like changing hormone levels in plasma, deformation of sexual organs or infertility. A further ecotoxicological effect of DDT pollution is egg shell thinning observed especially for birds of prey. However, the main problem of DDT contamination is related to its enormous tendency to accumulate in soils and sediments and also in biota. The bioaccumulation also along the food chain has been illustrated for the ecosystem of the Kariba dam lake as illustrated in Fig. 2.31.

Chlorinated hydrocarbons

DDT (insecticide)



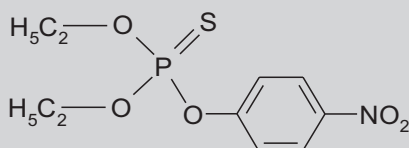
Water solubility: 🐼 (insoluble)

Half-life time in soil: 🐼 (several years)

➡ high risk of geoaccumulation

Thiophosphoric acid esters

Ethyl Parathion= E 605 (insecticide)



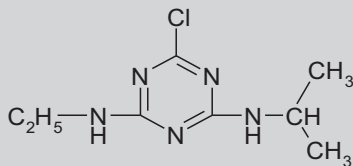
Water solubility: 🐼 (55 mg/L)

Half-life time in soil: 🐼 (several days)

➡ low risk for groundwater

Heterocyclic compounds

Atrazine (herbicide)



Water solubility: 🐼 (mg/L)

Half-life time in soil: 🐼 (several months)

➡ potential risk to groundwater

Fig. 2.27 Three pesticides, their relevant physico-chemical properties and the resulting risk assessment

Further on, due to its elevated geoaccumulation potential, areas of former industrial DDT-producing sites have become superfund sites, e.g. Palos Verdes Shelf (USA) or the Teltow Canal (Germany). Here, tremendous concentrations of up to 4000 ng/g have been found in the aquatic sediments pointing to a prolonged stability in particular under anaerobic conditions.

DDT has been synthesized commercially by a simple two-step Friedel-Crafts acylation using chloral and chlorobenzene (see Fig. 2.32). This reaction forms dominantly the 4,4'-chlorosubstituted isomer (or p,p'-DDT) but additionally the

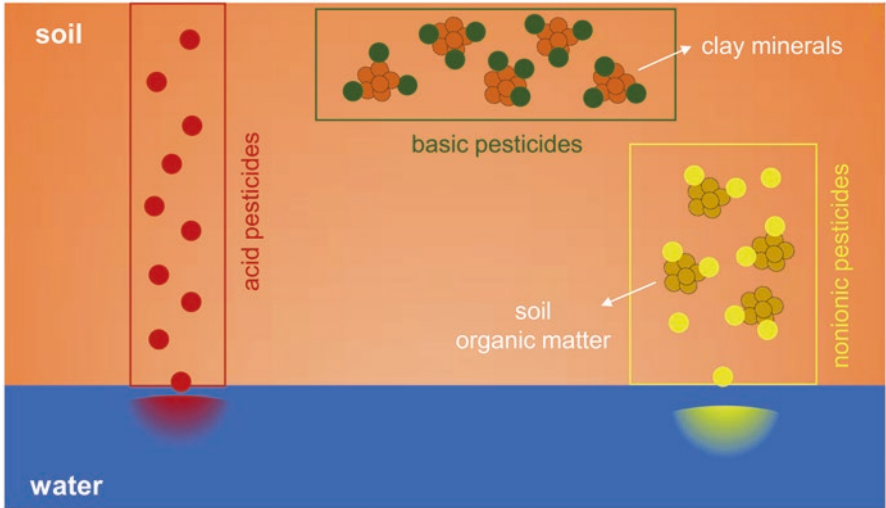


Fig. 2.28 Adsorption and mobility of pesticides with different chemical properties

Persistence of some pesticides in soil

chlorinated hydrocarbons	several years
urea derivatives	> 2 to 18 months
thiophosphoric acid esters	up to 12 weeks
carbamates	up to 12 weeks

Fig. 2.29 Rule of thumb for the environmental stability of different pesticide groups (According to Bliefert 2002)

2,4'-chlorosubstituted derivative (or o,p'-DDT) is synthesized. Hence, DDT contaminations normally consist of both isomers.

Noteworthy, DDT does not remain unaltered in the environment. The persistence of DDT is not attributed to the initial substance but more to its metabolites that exhibit a higher environmental stability. Consequently, assessing a DDT contamination needs implicitly to include the metabolites. Since highest geoaccumulation potential has been observed in aquatic sediments, the anaerobic metabolism is introduced shortly in Fig. 2.33. The primary transformations appear at the trichlormethyl group comprising successive dechlorination by elimination (forming double bonds) or reductive exchange with hydrogen forming saturated and unsaturated metabo-

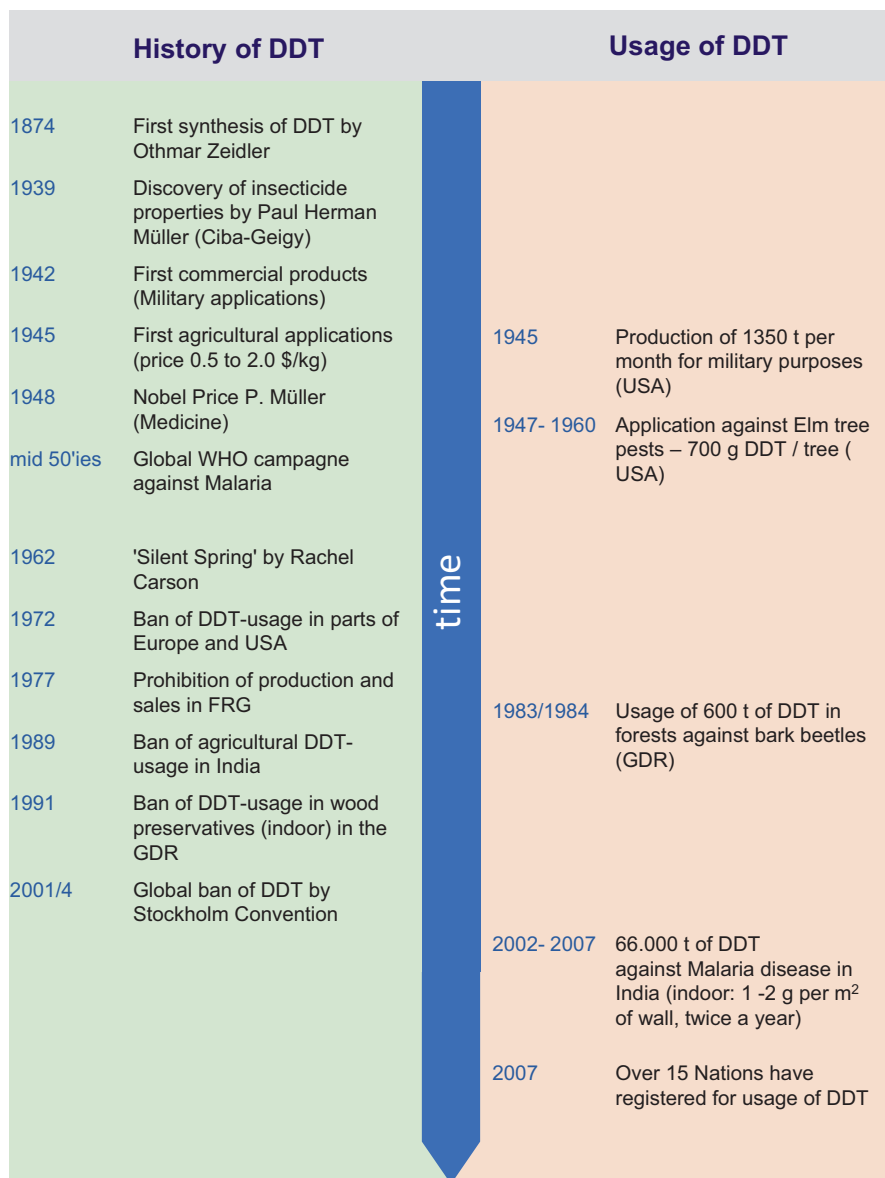


Fig. 2.30 History of DDT and its application

lites. At a second stage the methyl group becomes functionalized by hydroxy, carboxy or cyano groups. Thereafter, the modified methyl group gets cleaved and chlorinated diphenylmethane or benzophenone is formed. These compounds finally underlie a breakdown of the aromatic systems. During the metabolism, some derivatives exhibit much higher stability as compared to DDT. Under anaerobic conditions notably DDD is highly stable and the main constituent of DDT residues.

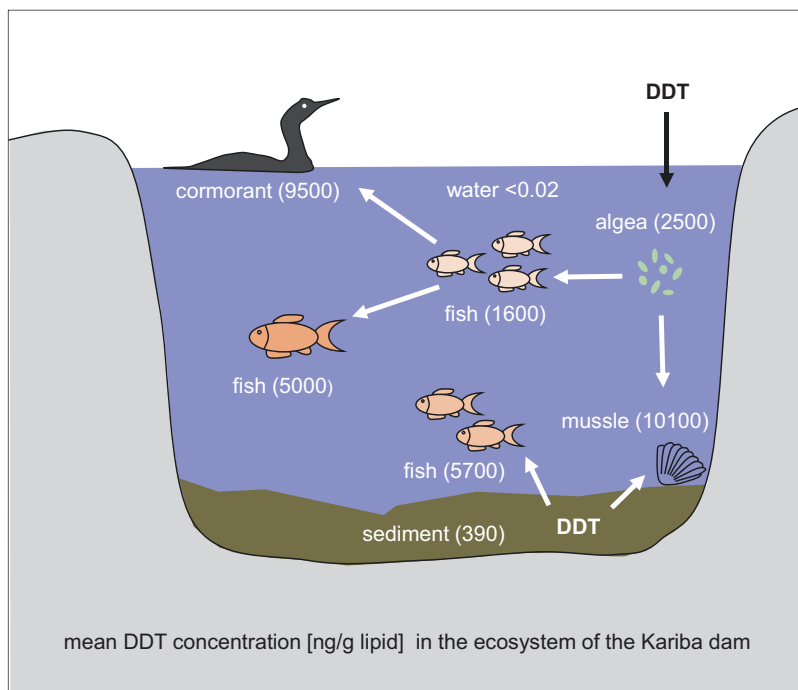


Fig. 2.31 Example of the bioaccumulation potential of DDT residues in the aquatic environment (Adapted from and modified after Alloway and Ayres 1996 and citations therein)

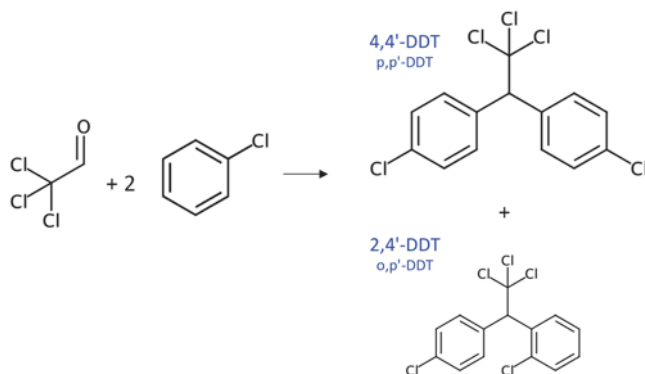


Fig. 2.32 Commercial DDT synthesis

This metabolism needs to be considered also for ecotoxicological assessments, since the metabolites exhibit different toxicological potential. As an example, the order of estrogenic effects of various DDT metabolites has been described as: *o,p'*-DDT > *p,p'*-DDMS > *p,p'*-DDMU > *p,p'*-DDCN. For cytotoxicity the following order has been reported: *o,p'*-DDT > *p,p'*-DDMU = *p,p'*-DDCN > *p,p'*-DDMS > *p,p'*-DDA (Schulze et al. 2003).

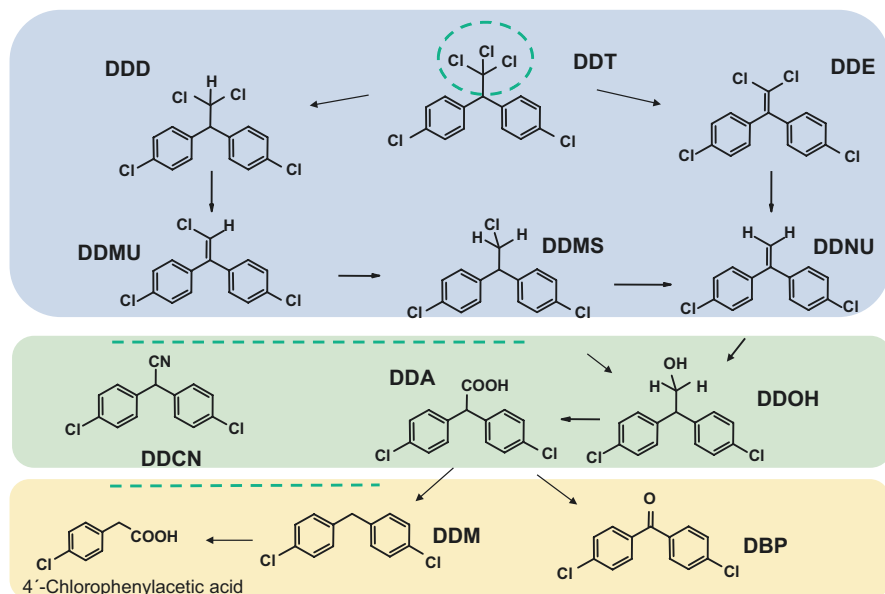


Fig. 2.33 Microbial DDT degradation under anaerobic conditions. Note the three different stages of the metabolism pathway

Secondly, the metabolites exhibit also different chemical moieties with different potential to form bound residues by covalent linkages. In Sect. 1.5 the covalent linkage of DDA, the acidic metabolite of DDT, has already been described. Comparing the metabolite spectra of the extractable or free fraction (dominated by DDD) with the bound residues (dominated by DDA), a distinct difference is obvious pointing to different tendencies to get incorporated into particulate matter for individual DDT derivatives (see Fig. 2.34).

A second pesticide out of the group of halogenated hydrocarbons is lindane. This pesticide has some interesting structural features that will be briefly introduced. Technical lindane synthesis is simply a photo-induced chlorination of benzene by Cl_2 . This process produces a mixture of stereoisomers of hexachlorocyclohexanes HCHs. These isomers differ in their relative positions of chlorine atoms at one carbon atom. Here, axial and equatorial positions have to be differentiated. The possible variations or isomers are named with Greek letters as prefixes, from α - to ϕ -HCH. Technically only α - to ϵ -isomers are generated with a dominance of α -HCH (see Fig. 2.35). Lindane is the γ -isomer. Noteworthy, only this isomer has insecticidal properties, all the other isomers have no effect on insects pointing to the importance of stereochemistry for toxicological effects.

In the first period of lindane application the technical mixture with only ca. 15% of active ingredient has been used. Later on, lindane has been separated from technical mixture and used as pure γ -HCH. During the purification step, huge amounts of HCH waste have been accumulated that have been partly deposited improperly.

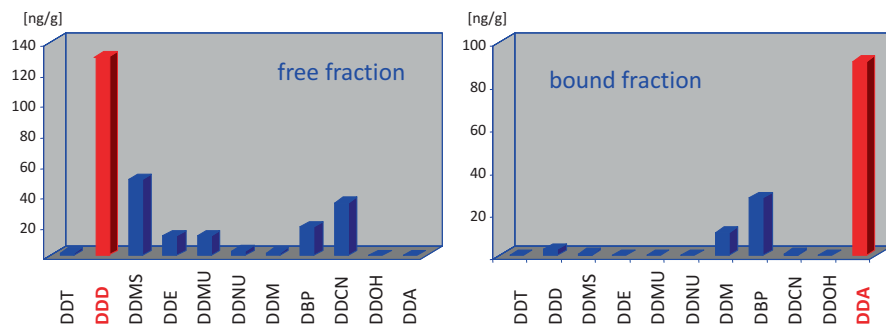


Fig. 2.34 DDT metabolites occurring in the extractable (free) fraction and the non-extractable (bound) fraction of an aquatic sediment (Data adapted from Schwarzbauer et al. 2003)

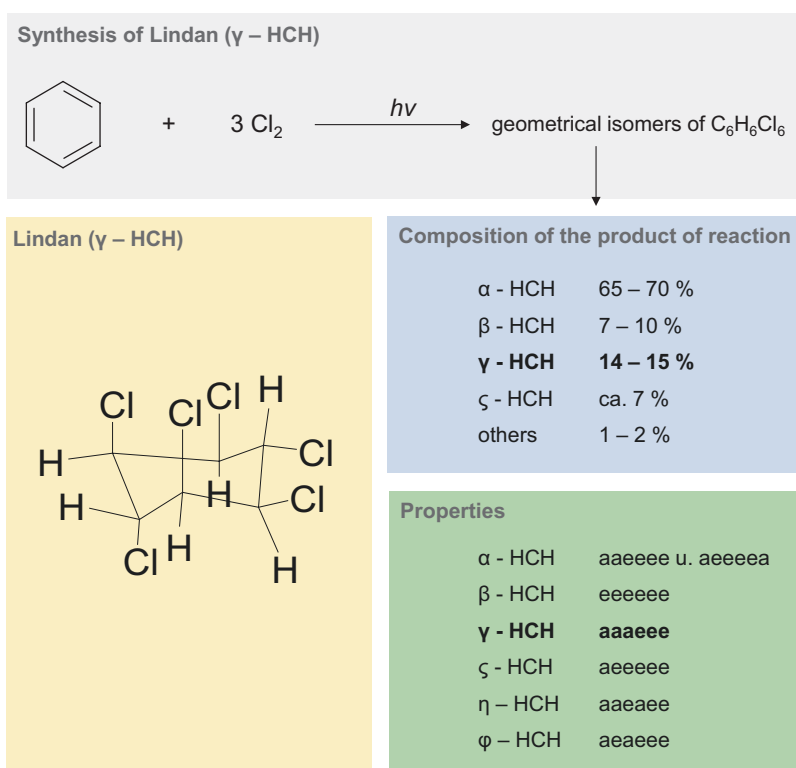


Fig. 2.35 Synthesis and stereochemical properties of hexachlorocyclohexanes including the insecticide lindane (γ -HCH)

They are many similarities to DDT. Lindane and HCHs accumulate dominantly in soils and sediments as well as in biota. Their environmental stability is also comparable to DDT and, therefore, they belong to the group of *persistent organic pollutants* POPs and have been banned by the *Stockholm Convention* (see Chap. 4).

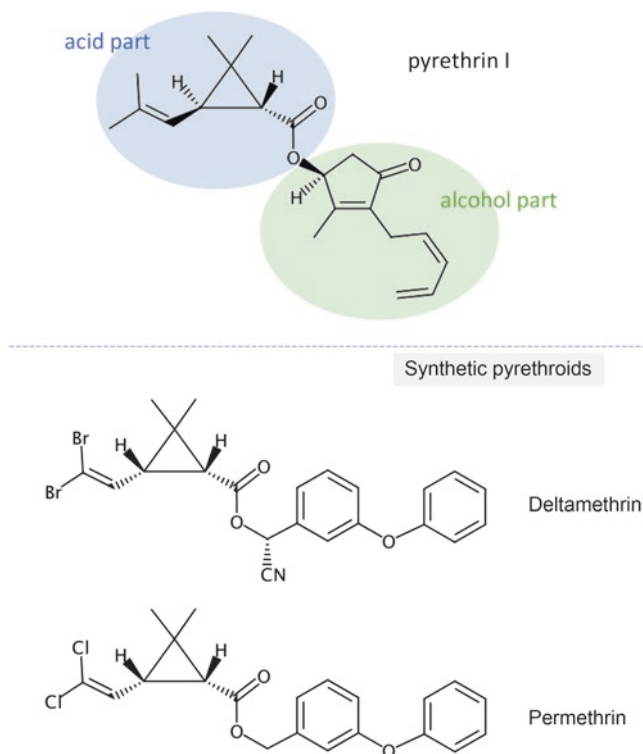


Fig. 2.36 The natural pyrethrin I and two representative synthetic pyrethroids

The moderate acute toxicity of lindane is accompanied by more relevant chronic effects in particular harming the nervous and immune systems. Lindane is also suspected to have carcinogenic properties. Generally, the α - and β -isomers exhibit some higher toxicities.

Lastly, a group of pesticides will be introduced briefly which has been developed by copying natural insecticides. In certain flowers (*tanacetum* and *chrysanthemum*) very effective substances against insects are known for millenniums. Their chemical composition and the structural properties of the active ingredients have been identified around 1925 to be esters of the (+)-*trans* chrysanthemic acid and one oxidized derivative. An example of such natural pyrethrin is given in Fig. 2.36. Pyrethroids are synthetic derivatives of these natural products that exhibit even higher insecticidal properties. Also two prominent synthetic pyrethroids are illustrated in Fig. 2.36.

With respect to environmental risks, two aspects must be noted. Although pyrethroids are harmless for mammals and humans, they are not only toxic for insects but also for aquatic organisms even in very low concentrations (see Table 2.7). Further on, they are not removed in sewage treatment plants. Hence, a pollution of surface water systems is evident with harmful effects for the aquatic environment.

Table 2.7 Some toxicity data of synthetic pyrethroids

	Birds	<i>Hyalella Azteca</i> (crustacea)	Rats	Mice	<i>Cyprinodon</i> <i>Variegatus</i> (fish)	<i>Daphnia</i> <i>Magna</i>
Pyrethroid	mg/kg b.w.	ng/g ¹ d.w.	mg/kg b.w.	mg/kg ⁻¹ b.w.	µg/L	µg/L
Permethrin	>13,500	100	1500	514	7.8	0.5
Fenvalerate	9932	–	–	245	5.0	1.2
Cyfluthrin	4450	15	–	–	–	0.17
Cypermethrin	–	–	250	–	1.0	2.0

Data taken from Alloway and Ayres (1996), Amweg et al. (2005), Cantalamessa (1993), Oikari et al. (1992), Bradbury and Coats (1989) and Thateyus and Selvam (2013)

2.3 Pharmaceuticals

Outlook

Due to their variable usage and their varying molecular structures, pharmaceuticals represent a relevant but also very diverse group of pollutants. Their emission pathways as well as their occurrence in the environment are discussed in this chapter.

Keywords Human pharmaceuticals • Veterinary pharmaceuticals • Antibiotics • Excretion • Aquatic environment

Pharmaceuticals are a group of physiological active substances widespread used not only for human but also veterinary medicine. These different fields of application imply different emission pathways for these compounds.

Basically, the incomplete assimilation and the corresponding excretion of administered pharmaceuticals are responsible for a permanent discard of these substances. For human usage, this results in emissions towards the sewage systems, but in case of veterinary applications emissions via slurry or dung are observed. Further on, an improper discharge of unused drugs by humans is responsible for further emissions towards sewage systems. Beside the contribution by domestic sources or livestock farming also the disposal of industrial waste has to be taken into account. A general scheme of emission pathways for pharmaceuticals is given in Fig. 2.37.

Pharmaceuticals discharged to sewage systems are subjected to waste water treatment but several compounds are not able to be removed completely and can enter partially the surface water systems. Veterinary drugs discharged via slurry are emitted directly to the soil and surface water environment. A further emission of pharmaceuticals can be attributed to fish farming and aquaculture also using pharmaceuticals for precautionary measures. Consequently, contaminations by environmental stable pharmaceuticals have been observed for surface water systems and soil/groundwater systems. Representatives of pharmaceuticals detected in the environment are illustrated in Fig. 2.38.

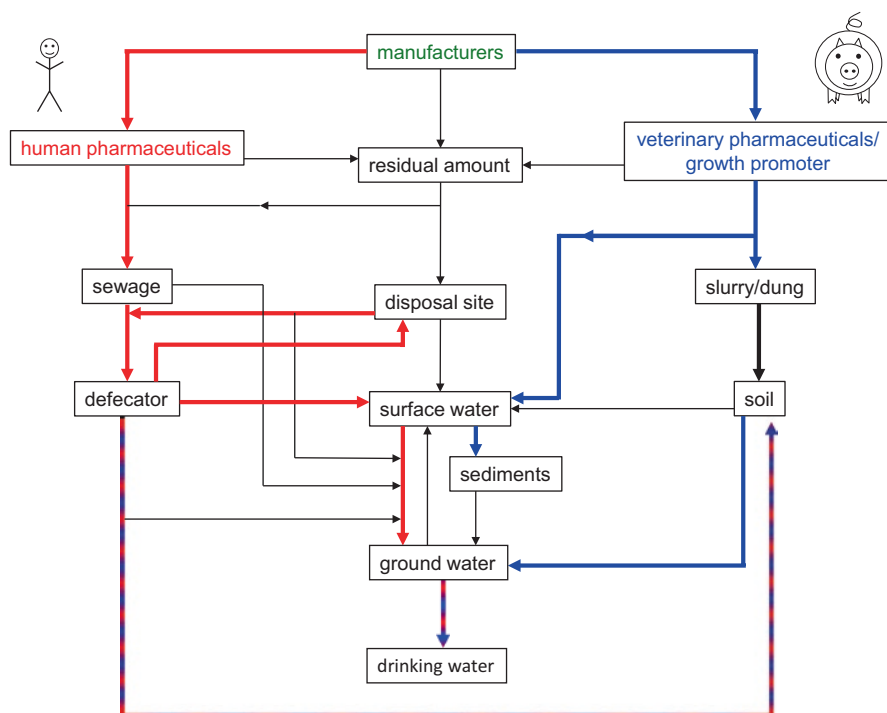


Fig. 2.37 General scheme of emission pathways for human and veterinary pharmaceuticals (Modified after Hirsch et al. 1999; Kümmerer 2001)

Pharmaceuticals in river water have been detected since the beginning 1970s. Increasing interest since the late 1990s resulted in a comprehensive description of these compounds in soils and surface waters, a selection of exemplifying data is given in Table 2.8. Noteworthy, the group of pharmaceuticals cover a very wide range of molecular structures and, correspondingly, a high variety of chemical and physico-chemical properties. This implies a big challenge in particular for the analytical detection of these compounds on environmental concentration levels.

When discussing the environmental occurrence of pharmaceuticals, one needs to consider different specific aspects. The intake of pharmaceuticals and their subsequent fate in organisms do not result necessarily in excretion of only unchanged substances. Often slightly altered metabolites are formed and excreted contemporarily. Additionally, the formation of conjugates (e.g. glyco-conjugates, see Sect. 1.3) are observed as a mechanism that is used by organism for an enhanced excretion. Metabolisation can be observed also during sewage treatment or even in the environmental compartments. However, the formed metabolites and conjugates have to be taken into account. This is exemplified for the pharmaceutical Ritalin in Fig. 2.39. Ritalin is not excreted by humans in its original form but as hydrolysis product, the ritalinic acid. An excretion rate of around 80% as ritalinic acid in human urine has been determined. After discharge towards the sewage systems, an insufficient elimination in waste water treatment plants by around 25% leads to an emis-

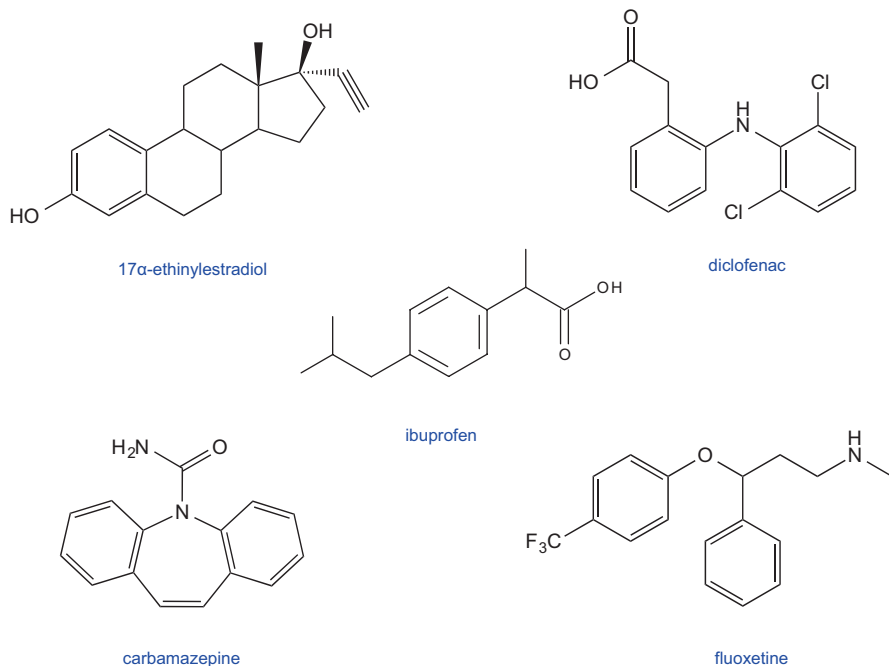


Fig. 2.38 A selection of pharmaceuticals frequently detected in the environment pointing to their enhanced environmental stability

sion towards riverine systems and, consequently, to the detection of ritalinic acid in river water. Noteworthy, this metabolite has been detected also in adjunctive river bank samples at concentrations on the same level as compared to river water. These findings point to an unhindered passage towards shallow groundwater and a risk for drinking water reservoirs.

Assessing the environmental relevance of pharmaceuticals needs a very distinct view on different aspects. This is tried to be figured out in Table 2.9 for representatives of a relevant class of pharmaceuticals, the antibiotics. Here, the potential amount of discharge is characterized by two parameters, the prescription amount and the excretion rate. Both parameters together give an idea about the relevance of individual antibiotics in terms of amount of potentially discharged residues. High prescription rates do not necessarily point to high discharge rates, but also high excretion rates are not exclusively relevant for quantifying the emission potential. Further on, the elimination in sewage treatment facilities is the second important aspect needed to be considered in estimating the environmental relevance of antibiotics. Here, also differences for the four selected representatives are evident in Table 2.9.

Table 2.8 Environmental data for pharmaceuticals detected in water systems

Compound	Concentration level (ng/L)	Water sample type	References
Acetaminophen	33–323	River water	Kim et al. (2007) and da Silva et al. (2011)
Acetaminophen	9.5–243	WWTP effluent	Kim et al. (2007) and da Silva et al. (2011)
Aspirin	4	River water	Kasprzyk-Hordern et al. (2008)
Atenolol	314–470	River water	Kasprzyk-Hordern et al. (2008) and Huerta-Fontela et al. (2011)
Atenolol	380	WWTP effluent	Huerta-Fontela et al. (2011)
Atenolol	2.3	Spring water	Benotti et al. (2009)
Atenolol	11–380	WWTP effluent	da Silva et al. (2011)
Carbamazepine	6–306	WWTP effluent	Huerta-Fontela et al. (2011), Vanderford and Snyder (2006), Kim et al. (2007), da Silva et al. (2011) and Ternes (1998)
Carbamazepine	4.1	Spring water	Benotti et al. (2009)
Carbamazepine	7–157	River water	da Silva et al. (2011), Huerta-Fontela et al. (2011), Kim et al. (2007), Kasprzyk-Hordern et al. (2008) and Vieno et al. (2007)
Diazepam	0.47	Spring water	Benotti et al. (2009)
Diazepam	3	River water	Huerta-Fontela et al. (2011)
Diazepam	0.3–3	WWTP effluent	Benotti et al. (2009), da Silva et al. (2011), and Huerta-Fontela et al. (2011)
Diclofenac	0.4–148	WWTP effluent	Andreozzi et al. (2003), Vanderford and Snyder (2006), Kim et al. (2007) and da Silva et al. (2011)
Diclofenac	3–24	River water	Kim et al. (2007), da Silva et al. (2011), Kasprzyk-Hordern et al. (2008) and Vieno et al. (2007)
Diclofenac	1.2	Spring water	Benotti et al. (2009)
Fluoxetine	1.7	WWTP effluent	Kim et al. (2007)
Fluoxetine	0.8	Spring water	Benotti et al. (2009)
Gemfibrozil	6.6	River water	Kim et al. (2007)
Gemfibrozil	11.2	WWTP effluent	Kim et al. (2007)
Gemfibrozil	2.2	Spring water	Benotti et al. (2009)
Ibuprofen	0.5–65	WWTP effluent	Lee et al. (2003) and Kim et al. (2007)
Ibuprofen	28–33	River water	Kim et al. (2007), Kasprzyk-Hordern et al. (2008) and Vieno et al. (2007)
Naproxen	11–53	River water	Kim et al. (2007), Kasprzyk-Hordern et al. (2008), Vieno et al. (2007) and da Silva et al. (2011)

(continued)

Table 2.8 (continued)

Compound	Concentration level (ng/L)	Water sample type	References
Naproxen	0.9	Spring water	Benotti et al. (2009)
Naproxen	87–128	WWTP effluent	da Silva et al. (2011) and Kim et al. (2007)
Paracetamol	968	River water	Kasprzyk-Hordern et al. (2008)
Quinolones	280	River water	Sun et al. (2015)
Sulfamethazine	160	Groundwater	Hirsch et al. (1999)
Sulfonamides	385	River water	Sun et al. (2015)
Trimethoprim	4–200	River water	Kim et al. (2007) and Kasprzyk-Hordern et al. (2008)
Trimethoprim	58–181	WWTP effluent	Kim et al. (2007) and Vanderford and Snyder (2006)
Trimethoprim	0.8	Spring water	Benotti et al. (2009)
Valsartan	24–685	River water	Kasprzyk-Hordern et al. (2008) and Huerta-Fontela et al. (2011)
Valsartan	690	WWTP effluent	Huerta-Fontela et al. (2011)

General Note

The environmental fate of pharmaceuticals is complex. In particular, metabolism, different excretion rates and varying environmental stability provide a very complex image of this pollutant group.

In the last decades, a more specific usage of pharmaceuticals in the aquatic environment gained high interest. Aqua farming has becoming a highly relevant economic business. Optimization of production rates were obtained *inter alia* by application of pharmaceuticals to prevent diseases and to improve the up growth. Some representative pharmaceuticals used in aquacultures are illustrated in Fig. 2.40.

For this field of application, a direct contamination of the environment is obvious. Beside direct emissions to the water body, aquaculture pharmaceuticals have been observed to accumulate concurrently in corresponding sediments as well as in biota such as water plants or mussels (e.g. norfloxacin and ciprofloxacin in sediments, fishes and water at Pearl river delta, China; He et al. 2012). Consequently, concentrations measured around aqua farming facilities reached elevated values (see Table 2.10).

Environmental impact of pharmaceuticals has been observed not only in the aquatic but also in the terrestrial environment. One example pointing also to the diverse and complex emission pathway and corresponding implications, was located in the Indian subcontinent. Here, a dramatic decrease of the vulture population has been observed in the 1990s and beginning 2000s. This decline of approx. 95% was obviously associated with symptoms of gout and kidney failure. A first clue on the cause of this environmental harm was observed by examining perished vultures.

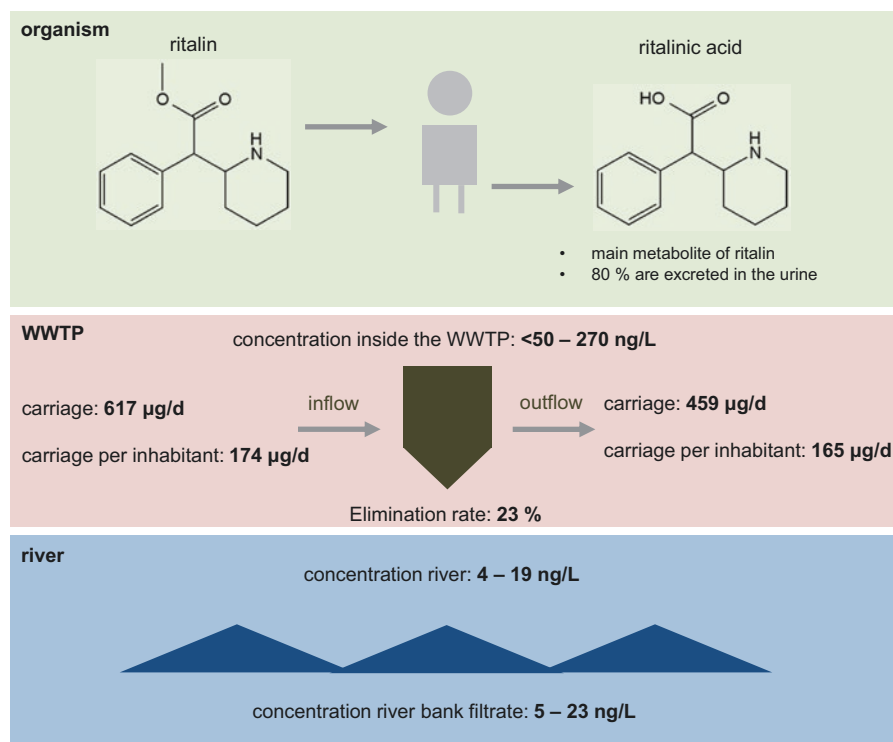


Fig. 2.39 Pathway, elimination rate and environmental detection of ritalin and its metabolite ritalinic acid, respectively (according to Letzel et al. 2010)

Table 2.9 Four antibiotics and their quantitative environmental assessment according to Hirsch et al. (1999)

Substance	Human prescription amount [d/a]	Human excretion rates of antibiotics [%]	Sewage treatment plant effluents – median [µg/L]	Examined surface water samples – median [µg/L]
Penicillin V	140	~40	n.d.	n.d.
Doxycyclines	8–16	>70	n.d.	n.d.
Sulfamethoxazoles	16.6–76	~15	0.40	0.03
Erythromycin	3.9–19.8	> 60	2.50	0.15

Analyses of different organs revealed notable residues of diclofenac in livers of those vultures that showed symptoms of gout (see Fig. 2.41). Feeding experiments confirmed the suspicion that diclofenac poisoning caused the threatening vulture extinction. The question remained how diclofenac has been taken up by the birds. Finally, it became aware that veterinary usage of diclofenac in cattle farming, an accumulation of the drug in the cattle and the tradition to leave dead cattle untreated in the environment for decay were the reasons for the poisoning. The vultures as scavenger took up the diclofenac by feeding on the cattle carrion.

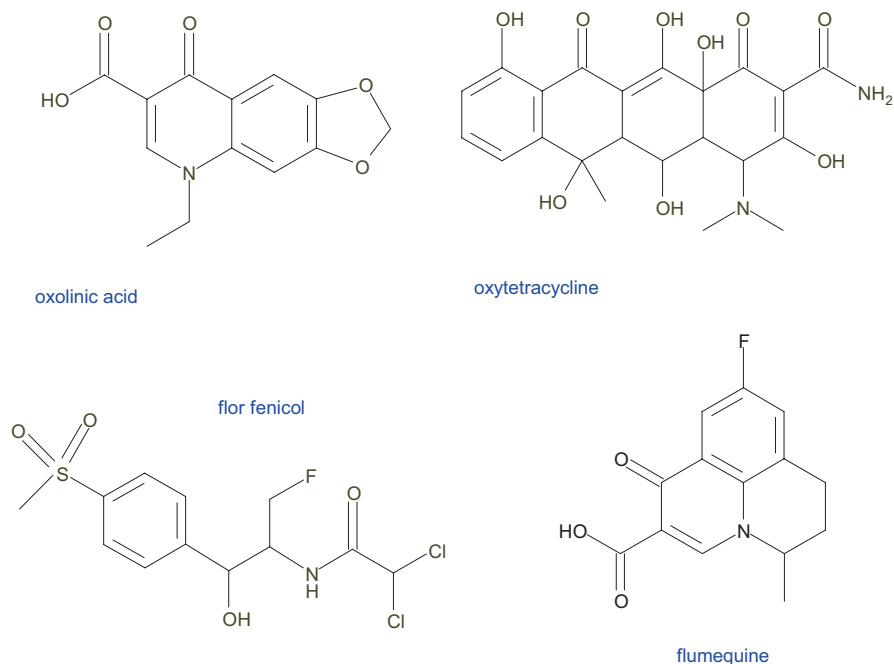


Fig. 2.40 Some pharmaceuticals commonly used in fish farming (according to Pouliquen et al. 2009)

Table 2.10 Antibiotics detected in fish farming and aquaculture

Antibiotics	concentration [μg/L]	References
Ciprofloxacin	0.022–0.2	Xiong et al. (2015) and Chen et al. (2015)
Enrofloxacin	0.017–0.021	Xiong et al. (2015)
Erythromycin	0.00001–0.00003	Munoz et al. (2010)
Metronidazole	0.013	Munoz et al. (2010)
Norfloxacin	0.026–6060	Xiong et al. (2015) and Le and Muneke (2004)
Oxytetracycline	0.022–15.13	Xiong et al. (2015) and Chen et al. (2015)
Sulfamethazine	0.006–0.036	Xiong et al. (2015)
Tetracycline	2.3	Chen et al. (2015)
Trimethoprim	0.0002–1040	Munoz et al. (2010), Le and Muneke (2004) and Lalumera et al. (2004)

Another important aspect regarding pharmaceuticals in the pedosphere is the usage of veterinary pharmaceuticals. Here a dominant pathway towards the environment is the contamination of slurry and manure by excretion of livestock containing residues of applied veterinary pharmaceuticals, often antibiotics. These substances are spread out as constituents of slurry used as fertilizer on agricultural soils. Correspondingly, elevated concentrations of such veterinary pharmaceuticals are detectable in many agricultural soils as exemplified in Table 2.11.

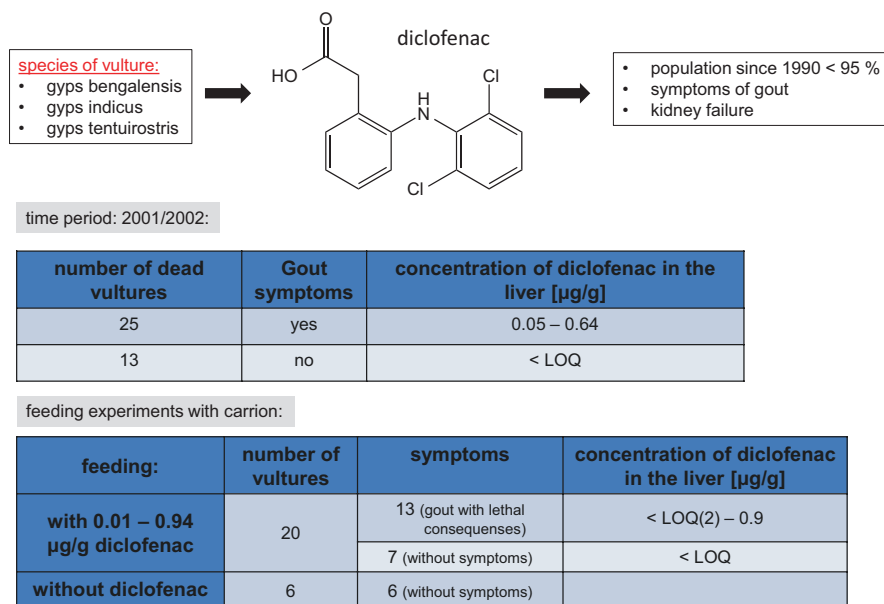


Fig. 2.41 Measurements and results of feeding experiments revealing diclofenac poisoning as main cause for vulture extinction in India (data adapted from Oaks et al. 2004)

Table 2.11 Antibiotics found in soil samples amended with sludge pointing to veterinary usage as main emission source

Antibiotic	Concentration (µg/kg)	Source
Tetracycline	22–443	Li et al. (2015), Pawelzick et al. (2004) and Hamscher et al. (2002)
Chlortetracycline	7–120	Hamscher et al. (2002), Li et al. (2015), Ostermann et al. (2013) and Pawelzick et al. (2004)
Oxytetracycline	27–423	Pawelzick et al. (2004) and Li et al. (2015)
Ciprofloxacin	38–253	Luo et al. (2011) and Li et al. (2015)
Enrofloxacin	62–389	Ostermann et al. (2013) and Li et al. (2015)
Sulfamethazine	1.7–110	Li et al. (2015), Pawelzick et al. (2004) and Ostermann et al. (2013)
Trimethoprim	20	Luo et al. (2011)
Sulfonamides	500	Schmidt et al. (2005)

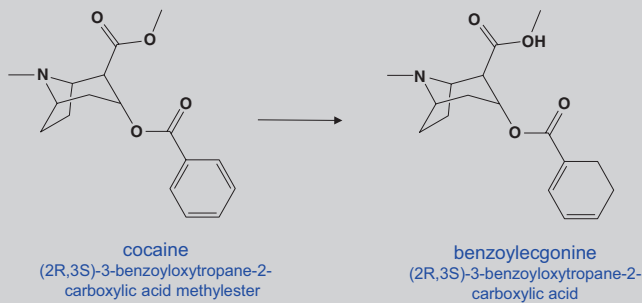
General Note

Due to the complex environmental behavior of pharmaceuticals the linkage of emission sources and effects observed in the environment are often not obvious. A comprehensive view on the environmental fate of pharmaceuticals is necessary to identify a reliable risk potential.

Excursion – Calculating drug abuse by environmental data

Environmental data can be used not only for environmental aspects, e.g. for risk assessment, but also for the quantitative estimation of usage, e.g. of pharmaceuticals and drugs. This has been applied for estimating the drug abuse of cocaine in the North Italian region by evaluation of data from the Po river (Zuccato et al. 2005). Beside cocaine especially its metabolite benzoylecgonine had been considered.

Based on the water concentrations and calculating the corresponding loads in the range of kilograms per day, the consumption of cocaine per 1000 inhabitants has been estimated to be around 0.7 g or 7 doses per day. Despite many uncertainties in such calculations, this example points to the possibility to recalculate usage rates from environmental data.



cocaine [ng/l]	benzoyl-ecgonine [ng/l]	equivalent cocaine loads [g/d]	cocaine [g/d]	doses	cocaine [g/d]	doses
			per 1000 citizens		per 1000 young citizens	
1.2 ± 0.2	15 ± 5	3800 ± 720	0.7 ± 0.13	7 ± 1.3	2.7 ± 0.5	27 ± 5

Germany:

Rhine around Düsseldorf (about 38.5 Mio citizens) : 11 t/a (30 kg/d)
statistic consumershare of the 18-59 year old people (about 23.5 Mio) : 0.8 %


- 
- 60 g/a (164 mg/d) per sonsumer
 - 411 mg or 16 line at 25 mg (with a shell of purity of 40 %)

Table: Cocaine and benzoylecgonine concentrations measured in water from the Po river (according to Zuccato et al. 2005) as well as calculation of consumption rates

2.4 Personal Care Products

Outlook

Personal care products are mixtures of various constituents partly exhibiting environmental relevance. Representative substance groups will be briefly introduced and discussed.

Keywords Surfactants • LAS • Nonylphenol • PFOS • Fragrances • Musks • UV absorber • Bactericides

In private life, a huge amount of personal care products and related products are used and discharged in particular to the sewage systems. These products are mixtures of various constituents with different functions, from which numerous substances are able to pass unaltered the sewage treatment facilities to a significant extent. Because of their release to the environment and due to partly ecotoxicological properties, these substances exhibit an environmental relevance.

Cleaning agents consist of several ingredients in various concentration levels. Main constituents are detergents, softeners and in some formulations bleaching systems. A general cleaning agent composition is given in Table 2.12. Most important agents are the surfactants but they account for only up to 10%, whereas main components are often builder components and softening agents. More specialized ingredients are bleaching agents as well as their stabilisers and activators (see Table 2.12), enzymes, optical brighteners or foam regulators. Lastly, fragrances represent only trace components with approx. up to 0.5%.

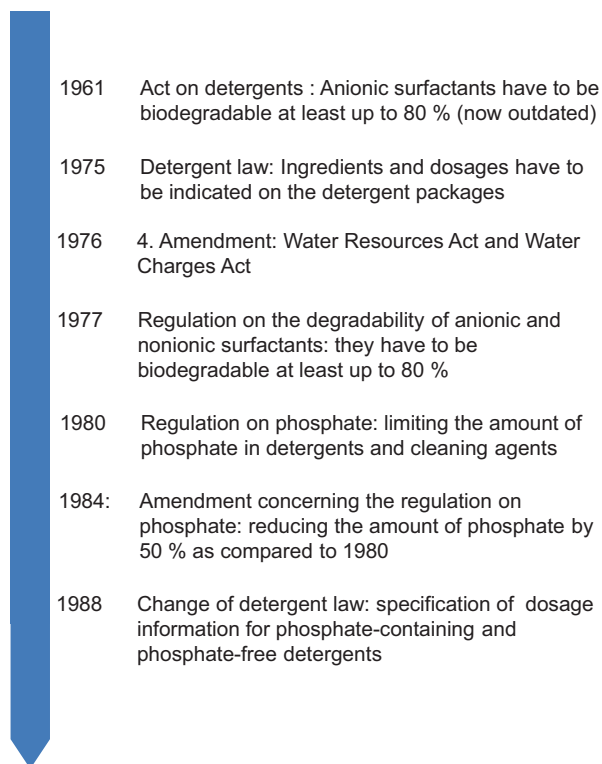
Negative effects due to the intensive usage of detergents especially for the aquatic environment are known for over 60 years. On the one hand, the visible effect of enhanced foam generation in surface water systems due to the elevated discharge of surfactants pointed to their environmental occurrence. On the other hand,

Table 2.12 Exemplary composition of cleaning agents

Ingredients	Example	Amount in %
Anionic surfactants	Alkylbenzene sulfonates LAS	5–10
Nonionic surfactants	Nonylphenol ethoxylates NPEO	1–5
Softener	Pentasodium triphosphate, zeolithes	10–40
Bleaching agent	Sodium perborate	15–35
Bleaching activators	Tetraacetylene diamine	1.5–4
Enzymes	Proteases	0.3–2
Redeposition inhibitors	Carboxymethyl cellulose	0.2–2
Discoloration inhibitors	Polyvinyl pyrrolidone	0.5–2.0
Foam regulators	Silicones	1–5
Optical brighteners	Stilbene- and pyrazoline derivates	0.1–0.5
Floating agent	Sodium sulphate	2–20
Fragrances	Citronellol	0.2–0.5

Data adapted from Bliefert (2002), Heintz and Reinhardt (1991) and references cited therein

Fig. 2.42 German regulations for detergents (modified after Heintz and Reinhardt 1991)



eutrophication processes as the result of increasing levels of phosphorus derived from detergents became evident in the 1960s. These obvious effects resulted in a very early regulation of detergent composition. Already in 1961, a first act in Germany stipulated a high biotic degradability of anionic surfactants of at least 80% (see Fig. 2.42). Following, this restriction became valid also for other types of surfactants. Concurrently, more transparent declarations of ingredients as well as clear instructions for dosage have been demanded. And lastly, the content of phosphates has been reduced stepwise till phosphate-free detergents have dominated the market.

Since these acts had clear consequences for the production and use of softening agent as well as for surfactants, these constituents are discussed in more detail in the following Sections (2.4.1 and 2.4.2). Finally, fragrances widely used in personal care products are introduced as relevant environmental contaminants in Sect. 2.4.3. Some more specific active components of personal care products are briefly introduced in Sect. 2.4.4.

General Note

Due to daily usage and following discharge via municipal sewage, these products can enter especially the aquatic environment, if they are not successfully retained in waste water treatment plants. The high usage volumes can imply a high threat for aquatic ecosystem.

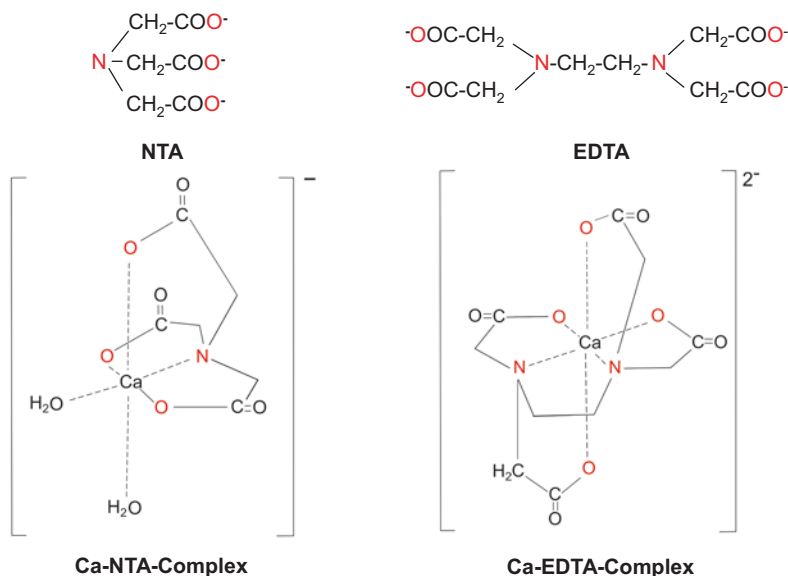


Fig. 2.43 Mechanism of calcium ion complexation by EDTA and NTA (modified after Heintz and Reinhardt 1991)

2.4.1 Softening Agents

As a first consequence of these regulations and acts, phosphate as the dominant decalcifier in former times have been rapidly substituted. Main substituents have been zeolites, natural and synthetic organic complexing agents (citric acid or EDTA) as well as pyrophosphate. Main task for decalcifier is the removal of Ca^{2+} ions from the suds, since these ions lower the effectiveness of surfactants by forming only slightly soluble calcium salts. Each surfactant molecule linked to a calcium atom cannot act as detergent.

The strategy to eliminate active calcium ions from the suds are either an inclusion of calcium ions in pores (e.g. by zeolites with fitting pores) or forming of calcium complexes. Complexing agents are either natural products (like citric or tartaric acid) or synthetic chelating agents like EDTA (ethylenediaminetetraacetic acid) or NTA (nitrilotriacetate). The later substances exhibit four to six sectors for fixation of the metal ion in an octahedral symmetry as illustrated in Fig. 2.43.

From an environmental point of view the synthetic compounds EDTA and NTA exhibit some significance due to their environmental stability and their toxicological properties (low acute toxicity but cytotoxic and genotoxic potential). Although a biotic and partly an abiotic (photolytic) degradation is known, waste water treatment plants do not completely remove these substances and, consequently, both compounds have been detected frequently in surface water systems. Exemplifying data are summarized in Fig. 2.44.

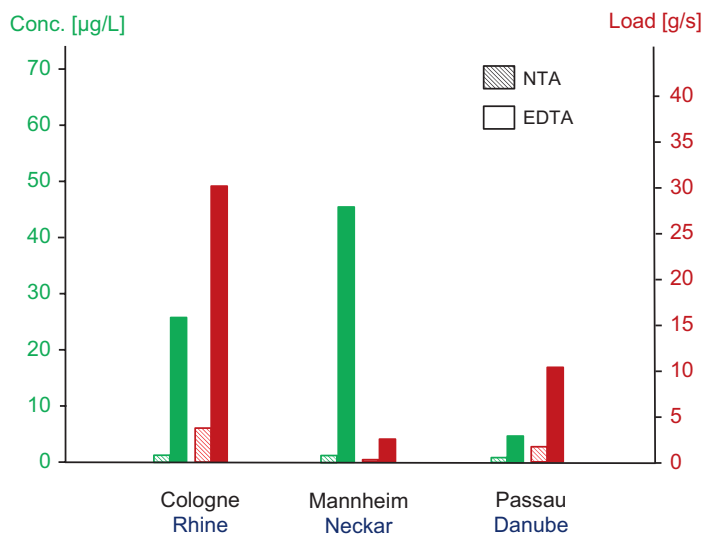


Fig. 2.44 EDTA and NTA concentrations and loads measured in selected German rivers (data taken from Frimmel et al. 1989)

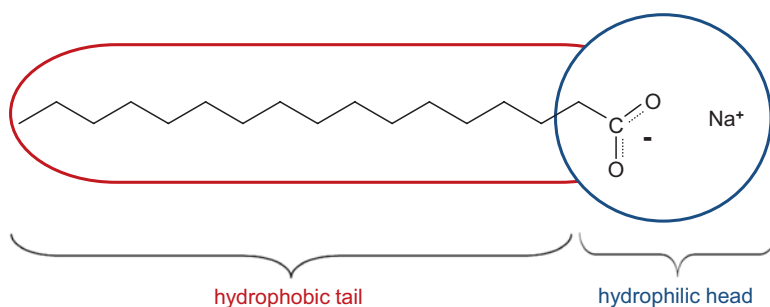


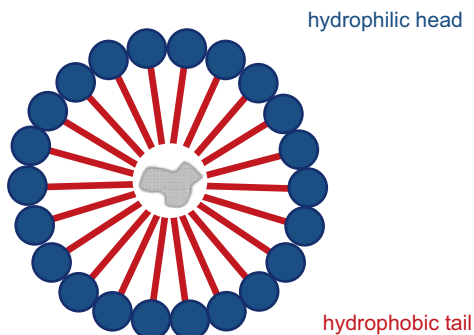
Fig. 2.45 Sodium salt of a fatty acid (a soap), an example for the principal molecular arrangement in surfactant molecules

2.4.2 Surfactants

Surfactants are responsible for washing processes. Generally, surfactants exhibit a specific molecular structure consisting of a smaller polar or hydrophilic part and a larger non-polar or lipophilic section (see Fig. 2.45). This principal structure represents an amphiphilic molecule and is a precondition to act as surfactant.

Principally, amphiphilic compounds enable a formation of emulsions since they encapsulate a lipophilic particle or drop with their lipophilic moieties forming a micelle. The polar groups are oriented towards the polar medium, e.g. water, and keeps the micelle in solution as illustrated in Fig. 2.46.

Fig. 2.46 Formation of micelles by amphiphilic molecules



The four main groups of surfactants (anionic, cationic, amphoteric and non-ionic surfactants) differ in their polar groups exhibiting either a cation, an anion, an amphoteric polar group or a polar but non-ionic group as exemplified in Fig. 2.47.

Surfactants act as main agents in the washing process. This can be depicted best by the washing process of clothes as illustrated in Fig. 2.48. Firstly, the dissolved amphiphilic molecules attach at the dirt surface (phase 1 + 2 in Fig. 2.48). At a certain density of attached surfactant molecules, the polar heads repel each other resulting in a split of the dirt particle and a break down into smaller pieces (phase 3 in Fig. 2.48). In a final phase, the dirt particles reach a size that provokes a detachment of the particles resulting in very small micelles (phase 4 in Fig. 2.48). As a secondary effect, surfactants adsorbed on the fiber hinder a re-adsorption of dirt particles on the tissue.

Most important detergents are anionic surfactants. Here, the alkylbenzenesulfonic acids are dominant (see Fig. 2.49) used in washing agents, toilet soaps, dish detergents or foam inhibitors. From a historical point of view, a first generation of these surfactants were synthesized using propylene as raw material for preparing approx. 12 carbon atoms containing aliphatics. Technically, four propylene molecules have been oligomerized forming a mixture of branched dodecanes (and to a lower extent also lower and higher homologues) which are following attached to a benzene ring via Friedel-Crafts alkylation. Finally, sulfonation was carried out with sulfuric acid. This synthesis pathway forms a complex mixture of branched aliphatic moieties and substitution isomers with respect to the linkage with the phenyl moiety. This resulting mixture is called tetrapropylene-based alkylbenzene sulfonates, ABS. Since branched aliphatic moieties are principally more difficult to be degraded by microorganisms, the biotic degradation potential of these surfactants is low. As a consequence of the regulations pointed out above, these surfactants needed to be replaced by better degradable substituents. In the 1960s, this led to the introduction of non-branched and, therefore, better degradable derivatives with highly similar structural properties, the so-called linear alkylbenzene sulfonates, LAS. The technical synthesis remained very similar (see Fig. 2.49), but the aliphatic moieties were regular without branches and were better biodegradable. Further on, the isomer mixture became simpler. Only isomers for phenyl substitution and homologues series with differing chain length were obtained.

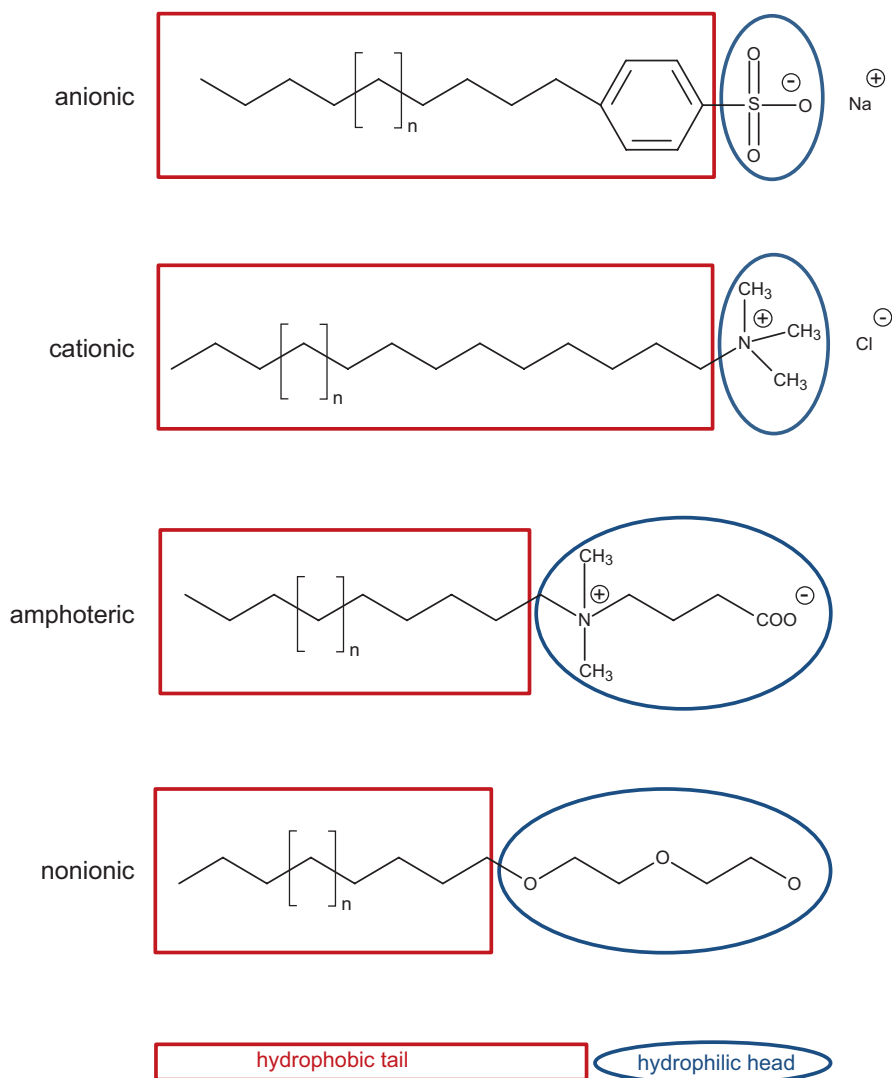
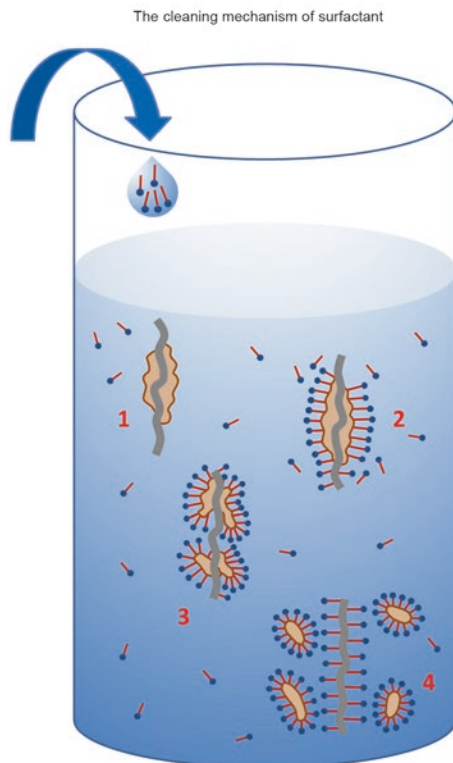


Fig. 2.47 Principal structure of the four principal groups of surfactants (according to Bliefert 2002)

The principal degradation pathway of LAS is given in Fig. 2.50. Here, the shortening of the non-branched aliphatic chain as essential degradation step is clearly visible. Further important transformation steps are the phenyl ring *meta*-cleavage and the desulfonation at a later step.

As for many other detergents, personal care products and further household products, the main discharge pathway is via the sewage systems. Although the microbial degradation is enhanced for LAS as compared to TAS, a total elimination in sewage treatment plants is not achieved and, consequently, sewage effluents are

Fig. 2.48 Scheme of washing process with surfactants (modified after Heintz and Reinhardt 1991)

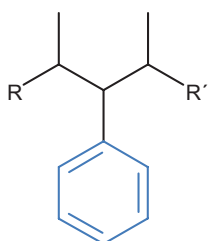


the main emission sources for these compounds. Considering additionally the high usage rate of surfactants, it is not surprising that alkylbenzene sulfonates can be detected in the aquatic environment.

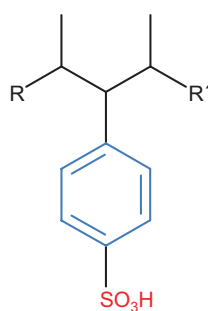
Beside the amphiphilic compounds ABS and LAS, the non-functionalized derivatives TAB and LAB are of environmental interest. The last technical synthesis step, the sulfonation, is not a 100%-reaction but has yields of only around 90%. Hence, up to 10% of the alkylated benzenes remain as byproducts. These byproducts are not removed from the technical mixtures and are not only ingredients in the commercial products but are also discharged to the environment accompanied with the surfactants. However, since alkylated benzenes exhibit an enhanced lipophilicity, these compounds tend to accumulate in the particulate matter of the aquatic systems, the suspended particulate matter and finally in the sediments. High environmental stability and geoaccumulation potential of LABs led to their usage as anthropogenic marker (Eganhouse et al. 1986). This is described in more detail in Chap. 5.

A second more modern group of anionic surfactants comprises fluorinated substances. The lipophilic moieties are built up here by perfluorinated carbon chains attached to polar end groups like hydroxyl, carboxylic acid or sulfonic acid groups. Principal molecular structures of this group of surfactants, often named as perfluoroalkyl compounds PFC, are given in Fig. 2.51.

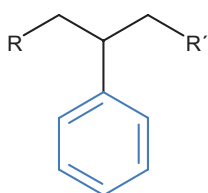
TAB's
tetrapropylene-based alkylbenzene



ABS
alkylbenzene sulfonate



LAB's
linear alkylbenzene



LAS
linear alkylbenzene sulfonate

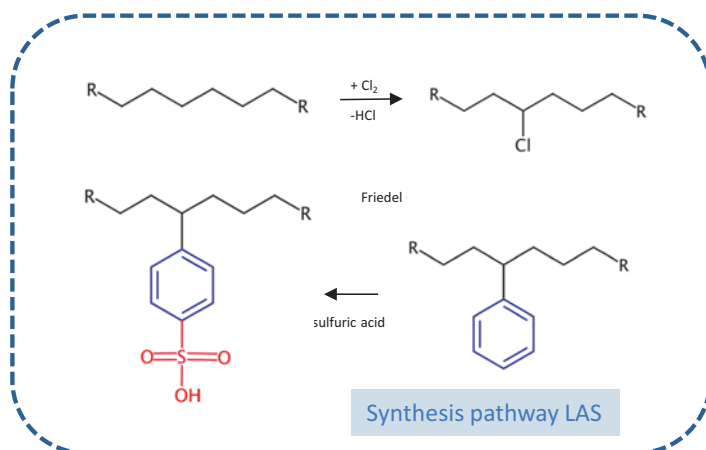
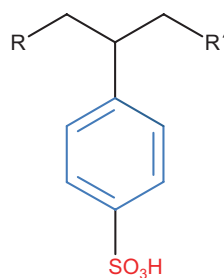


Fig. 2.49 Structural properties of ABS and LAS as well as their technical byproducts TABs and LABs. Additionally, the principal technical synthesis pathway for LAS is illustrated

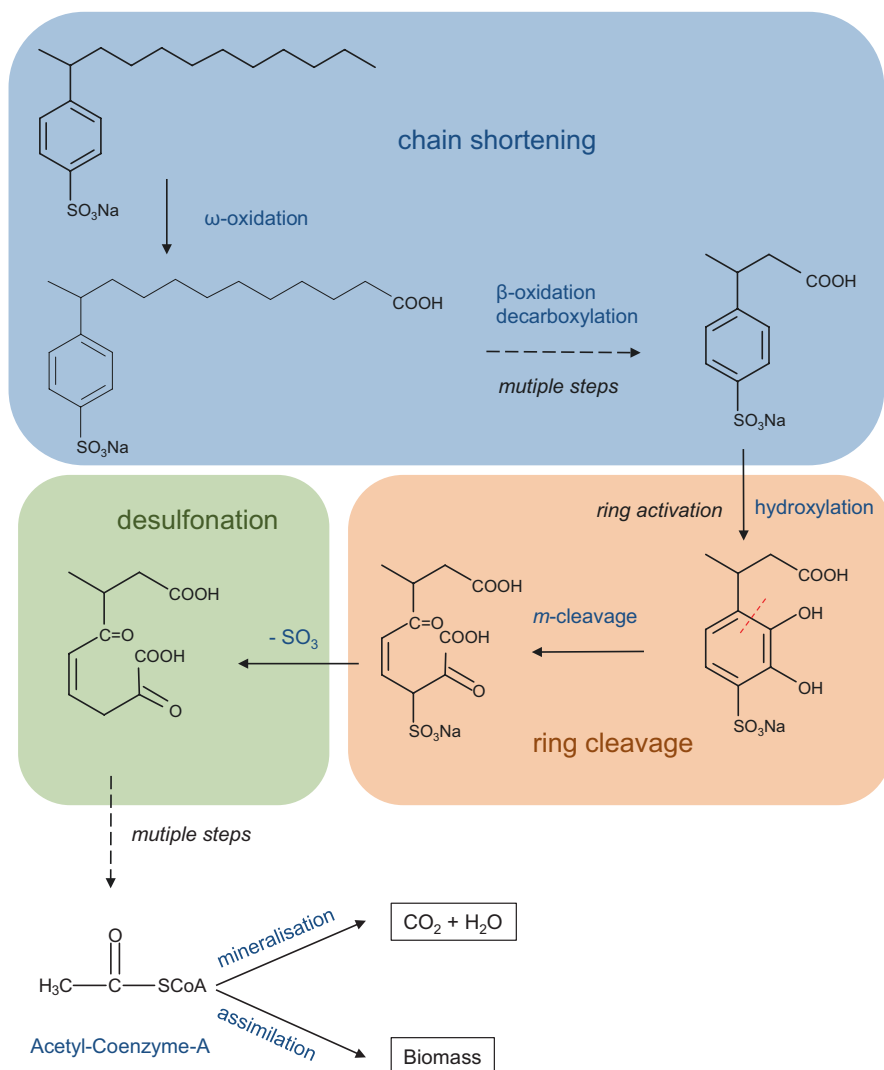


Fig. 2.50 Principal aerobic biotic degradation pathway of LAS (modified after Heintz and Reinhardt 1991)

The risk potential of these surfactants is related to their high environmental stability and their tendency for bioaccumulation. This is reflected by the environmental concentrations measured in various matrices. Some exemplifying data are given in Table 2.13.

Beside anionic surfactants also non-ionic substances play an important role in detergent chemistry. The production and usage rates of non-ionic and anionic detergents are on the same level, whereas cationic or amphoteric detergents are produced with rates approx. 10 times lower. Within the group of nonionic surfac-

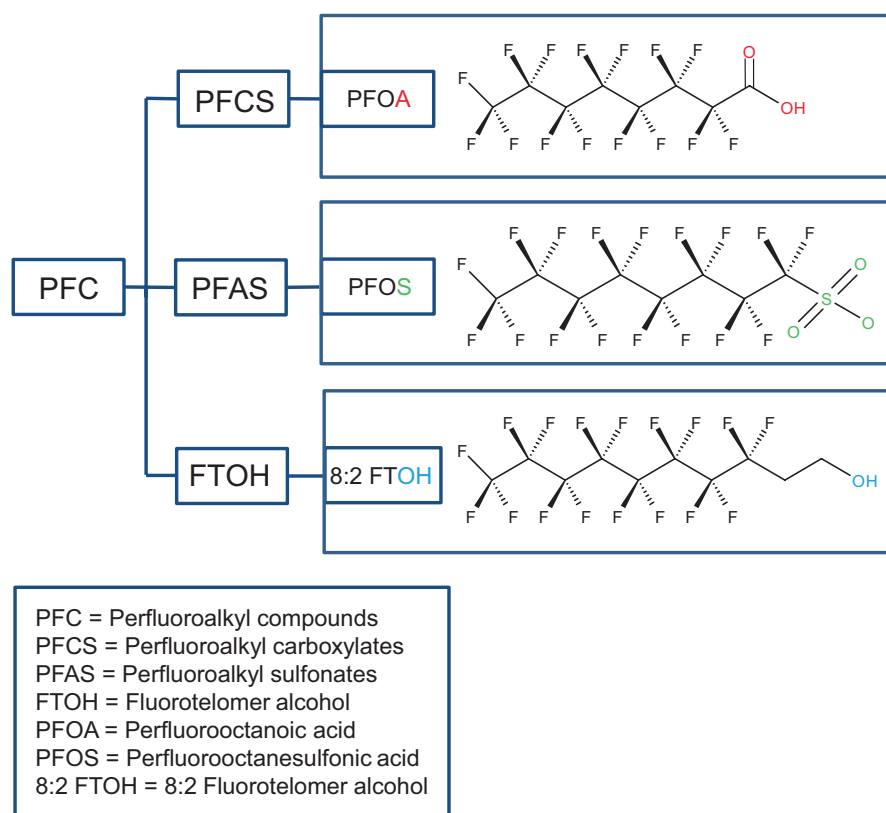


Fig. 2.51 Classification and representatives of perfluorinated compounds PFC acting as surfactants

Table 2.13 PFOS and related PFCs analyzed in various environmental matrices

Sample	Concentration	References
River water	36–700 ng/L	Pan and You (2010)
River sediment	72–530 ng/g	Pan and You (2010)
River water	82–260 ng/L	Wang et al. (2013)
River sediment	75–457 ng/g	Wang et al. (2013)
Common seabass (lateolabrax japonicus)	4–144 ng/g	Taniyasi et al. (2003)
Marine water	8–59 ng/L	Taniyasi et al. (2003)
Dust (appartments)	2–1200 ng/g	Björklund et al. (2009)
Dust (daycare centers)	20–90 ng/g	Björklund et al. (2009)

tants, especially the nonylphenol ethoxylates are environmentally relevant. The polar head is formed by alternating ethylenoxide groups with partial negative polarity at the oxygen moieties. They are also widely used, e.g. in washing or cleansing agents.

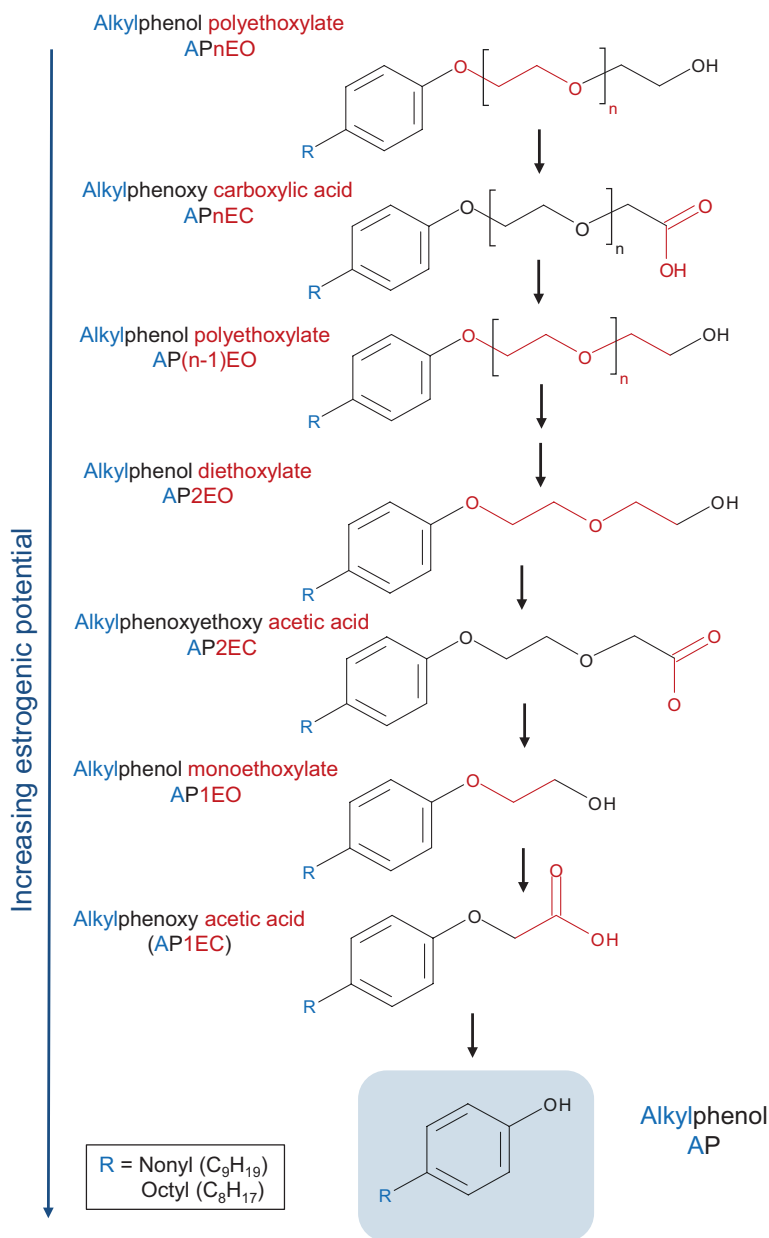


Fig. 2.52 Principal degradation pathway of nonylphenol ethoxylates. Chain shortening occurs via oxidation and loss of acetic acid

The most relevant environmental impact is not associated with the original commercial products but with their metabolism. The degradation pathway as given in Fig. 2.52 is simply a shortening by ethylene oxide moieties via oxidation and following release of acetic acids moieties. The corresponding metabolites are system-

atically named indicating the number of remaining ethylene oxide moieties and the end group, illustrated in more detail in Fig. 2.52. Noteworthy, the elimination rate of nonylphenol ethoxylates in sewage treatment plants is insufficient and, consequently, the original surfactants and all metabolites are detectable in sewage effluents as well as surface water systems, partly with concentration in the $\mu\text{g/L}$ range.

An important intermediate of the degradation pathway is nonylphenol, the transformation product after a complete removal of ethylene oxide moieties. Noteworthy, the term nonylphenol summarizes a mixture of branched nonyl moieties attached to the phenol ring at 4-position. These compounds are stable, especially adsorbed on particles and under anaerobic conditions. Therefore, an accumulation e.g. in aquatic sediments can be observed contrarily to the occurrence of the precursors dominantly in the water phase. Beside this changing environmental behavior, nonylphenol are also of higher toxicological concern since they are known to exhibit distinct endocrine disrupting properties. As a rule of thumb, the potential to act as endocrine disruptor increases along the degradation pathway of nonylphenol ethoxylates as indicated in Fig. 2.52.

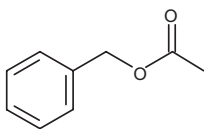
2.4.3 *Fragrances*

Fragrances are only trace components in personal care products. However, some representatives have some interesting environmental implications. Generally, natural and artificial fragrances have to be differentiated. This is exemplified for jasmine fragrances in Fig. 2.53. Main components like benzylbenzoate (25%) are no odorant. Natural fragrances in jasmine oil represent only less than 5% in total of the jasmin oil and comprises e.g. jasmone and various jasmonates. These compounds are similar but not identical to synthetic jasmine odors like methyl dihydrojasmonate.

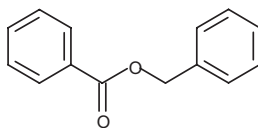
The same accounts for another very important flavor, the musk fragrance. Originally, various animals produce secretions smelling very similar, which is the typical musk odor (see Fig. 2.54). Main biological source for former musk compositions has been the musk deer. The composition of the musk odor is a mixture of various, dominantly cyclic substances, partly with nitrogen-containing aromatic moieties (pyridines). Synthetic musk fragrances differ significantly regarding their molecular structure.

Synthetic musks can be roughly divided into three classes related to their chemical structures but also to the time of commercial launch. These groups comprise nitro, polycyclic and macrocyclic musks (see Fig. 2.55). From an environmental point of view, only the first two groups are of interest. The first group, nitro musks, represents also the first generation and the components exhibit up to three nitro groups attached to monoaromatic systems (see Fig. 2.56). Although functionalized with polar groups, they exhibit a high environmental stability and a high tendency for geo- and bioaccumulation. Further on, they are only removed insufficiently dur-

Main components of jasmine oil

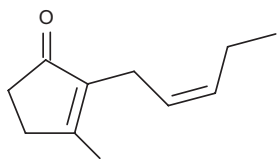


benzyl acetate (30%)

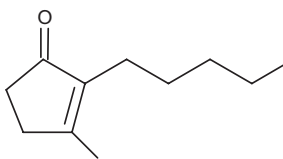


benzyl benzoate (25%)

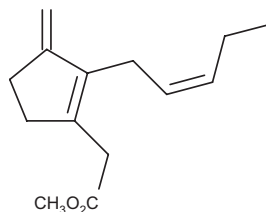
Natural jasmine fragrances (< 5%)



jasmone

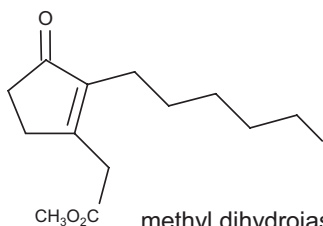


dihydrojasmone

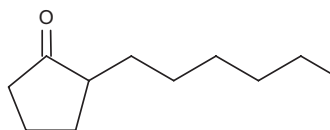


methyl jasmonate

Synthetic jasmine fragrances



methyl dihydrojasmonate



jasmatone

Fig. 2.53 Jasmine oil ingredients and jasmine fragrances

ing sewage water treatment. The accumulation and persistence e.g. of musk xylene classified it as 'substance of very high concern' according to the REACH system of the EU (see Chap. 1). However, nitro musks have been produced and applied intensively since 1900 but nowadays they are used only to minor extent dominantly in cosmetics.

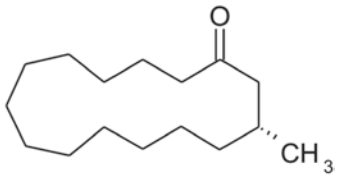
Natural sources of musk	<ul style="list-style-type: none"> • Musk deer
Natural sources of musk-like odors	<ul style="list-style-type: none"> • Musk rat • Musk duck • Musk ox • Musk beetle • Musk turtle
Compounds of musk	<ul style="list-style-type: none"> • Muscone • Muscopyridine • 2,6-Nonamethylenpyridine • 2,6-Decamethylenpyridine • 3-Methylcyclotridecanone • Cyclotetradecanone • 5-cis-Cyclotetradecenone • 5-cis-Cyclopentadecenone • 14-Methyl-5-cis -cyclopentadecenone • Muscol
Primary contributor to the odor of musk	<ul style="list-style-type: none"> • Muscone with 0.5 to 2 % 

Fig. 2.54 Biological sources and information on composition of musk

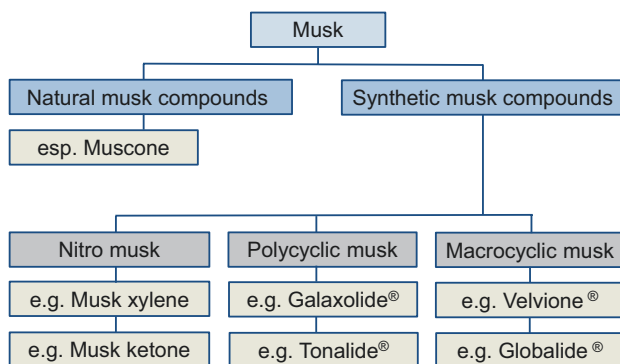


Fig. 2.55 Classification of musk with a special focus on the artificial musk fragrances

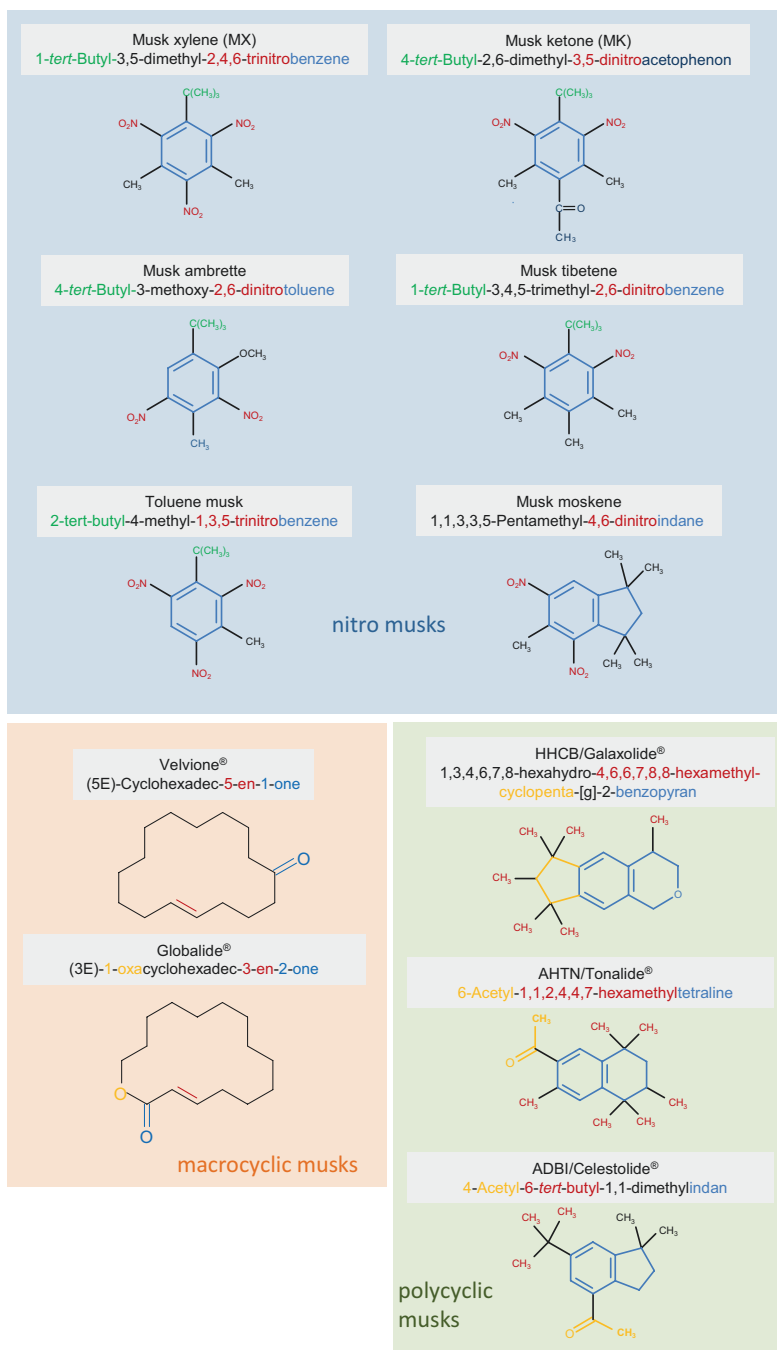


Fig. 2.56 Molecular structures of synthetic musks

Excursus – The discovery of synthetic musk fragrances

The first synthetic musk fragrance has been discovered by chance. Originally, the German chemist Baur tried to synthesize a new explosive (following the synthesis of TNT, see Sect. 2.7) via nitration of a *tert*-butyl substituted toluene. The result was a substance with only a moderate tendency to explode but with a very specific odor, the first synthetic musk – *musk xylene*.

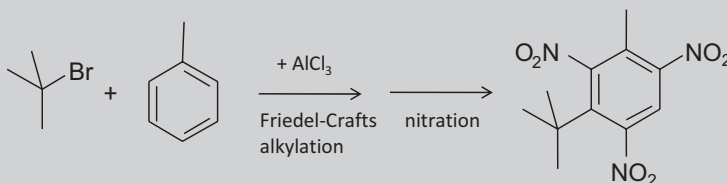


Figure: First synthesis of *musk xylene*

A second generation of musks are represented by polycyclic substances. The two main compounds are galaxolide and tonalide (see Fig. 2.56) widely used in fragrances and other household and personal care products as exemplified in Table 2.14. These compounds exhibit less potential for accumulation and their (eco)toxicological relevance is low. However, their intensive usage since the late 1960s and their low removal during sewage treatment led to a widespread detection of these odors in particular in the aquatic environment. Some environmental data are given in Table 2.14.

Table 2.14 Environmental data of musks

	Frequency in personal care products	Concentrations in STP effluents	Concentrations in surface water systems	Concentrations in human tissue
Musk ketone		<1–5000 ng/L	<5–390 ng/L (Berlin area, Germany)	5–30 ng/g fat
HHCB, galaxolide	perfumes: 86%	150–1600 ng/L	10–180 ng/L (Lippe river, Germany)	40–190 ng/g fat
	shower gel: 64%			
	deodorants: 100%		<3–600 ng/L (Ruhr river, Germany)	
	shampoos: 92%			
AHTN, tonalide	perfumes: 43%	50–1100 ng/L	5–70 ng/L (Lippe river, Germany)	19–33 ng/g fat
	shower gel: 14%			
	deodorants: 75%		<3–120 ng/L (Ruhr river, Germany)	
	shampoos: 33%			

Data adapted from Heberer et al. (1999), Dsikowitzky et al. (2002), Ricking et al. (2003), Bester (2005) and Reiner and Kannan (2006)

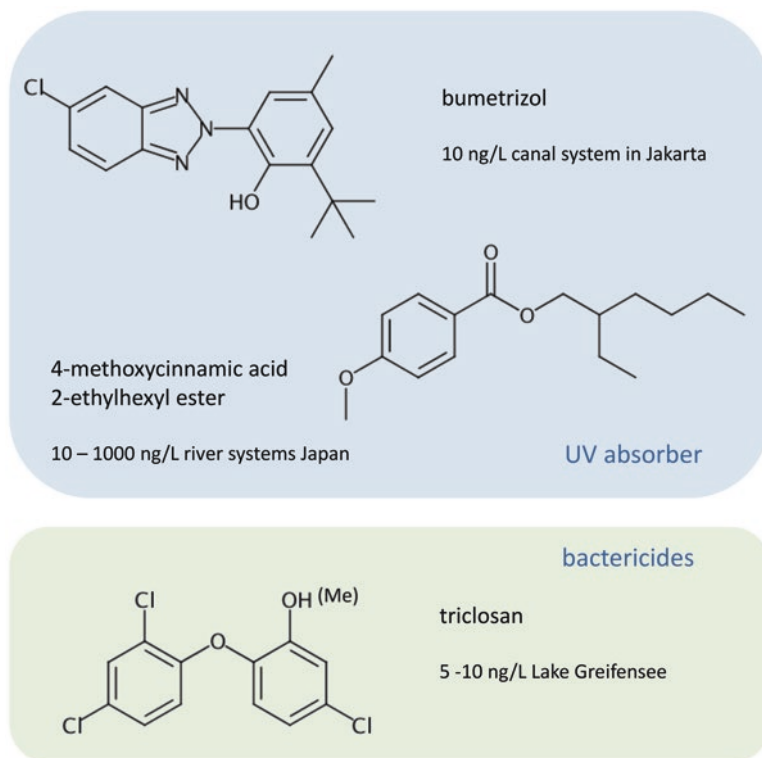


Fig. 2.57 Molecular structures and some environmental data of UV absorber and bactericides (Data taken from Singer et al. 2002; Kameda et al. 2011; Dsikowitzky et al. 2016)

2.4.4 Miscellaneous Ingredients

Finally, it should be noted that the spectra of ingredients in personal care products with environmental relevance is not fully covered by the compounds introduced so far. Further compounds are characterized by a high diversity in molecular structures as well as in care effects. From two groups with a more specific field of application, the UV absorbers and bactericides, a few representatives will be presented very briefly.

UV absorber are constituents not only of sun creams but also of many cosmetics. As examples, 4-methoxycinnamic acid 2-ethylhexyl ester (Parsol MCX[®]) and bumetrizol as UV-B absorber are depicted in Fig. 2.57. A second group covers the bactericide also ingredients in personal care products e.g. in tooth paste or shampoos. Interestingly, triclosan becomes biomethylated in the aquatic environment and the resulting methyltriclosan tends to adsorb on particles (sediments or suspended particulate matter).

All these constituents have been detected in the environment due to their field of application and their resistance against sewage treatment processes. Exemplifying data are given in Fig. 2.57.

2.5 Plasticizers and Further Technical Additives

Outlook

Technical additives are structurally diverse and are used in complex applications. Here only some examples are introduced pointing to the environmental relevance of this compound group.

Keywords Phthalates • Mesamoll • DIPN • Photoinitiators • Organophosphates

Numerous xenobiotics have been synthesized for a wide range of so-called technical application. These are additives used in technical processes or as constituents in products for improving their quality. Examples are plasticizers in polymers effecting a higher elasticity or UV inhibitors protecting against photolysis to extend the life time of the plastics. These substances cover a wide range of structural properties. According to their complex field of applications they are emitted to the environment by municipal but also by industrial emissions. Some examples of such substances and their environmental fate as well as their relevance are presented.

A first group of technical additives comprises plasticizers that are added especially to synthetic polymers to optimize the mechanical properties such as the elasticity of polymer products like foils or tubes. Best known plasticizers in terms of environmental characterization are phthalates. The esters of phthalic acid with *n*- and *iso*-butyl as well as 2-ethylhexyl moieties are the most common ones and important additives in PVC and synthetic gums. The most important compound is bis(2-ethylhexyl)phthalate also named DEHP. As emission pathway for plasticizers, the migration from polymer products into the water phase as well as the adsorption on particles e.g. dust, is described. Due to the very high production rates and the wide distribution of polymers, phthalates are now ubiquitous. Phthalates are identified to be endocrine disruptors leading to a substitution of these additives by alternative plasticizers.

Beside phthalates also singular compounds have been developed and applied as plasticizers. NBBS (N-butylbenzenesulfonic acid amide) has been widely used but its application has been stopped when neurotoxic effects became obvious. However, NBBS is still detectable in the environment. Also TXIB (2,2,4-trimethyl-1,3-pentandioldiisobutyrate), a PVC plasticizer, can be observed in particular in the aquatic environment (see Fig. 2.58). Lastly, the cyclic compound HMMM (hexa(methoxymethyl)melamine) has been detected in river water at elevated concentrations but also with highest loads. In 2001, HMMS loads of up to 60 kg/day have been analyzed in the Rhine river, Germany (Dsikowitzky and Jan Schwarzbauer 2015).

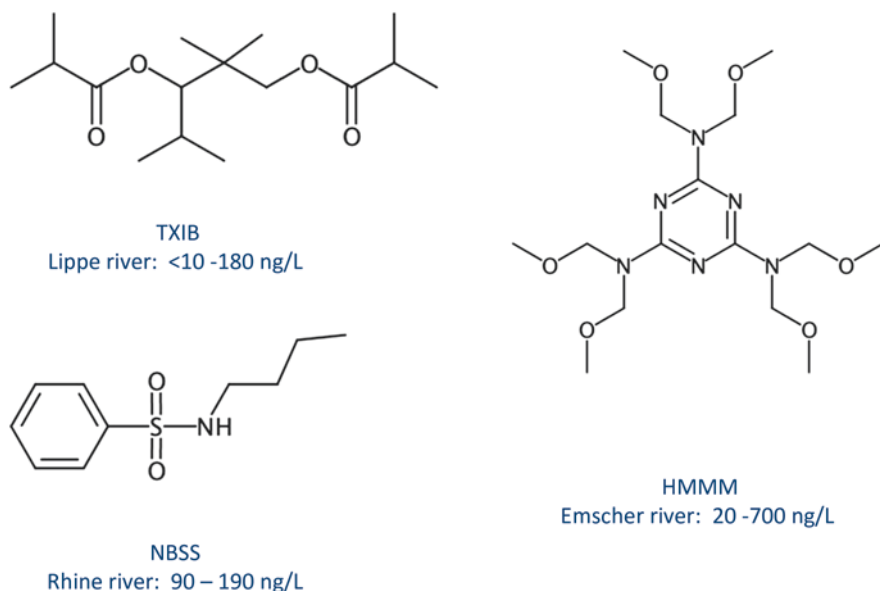
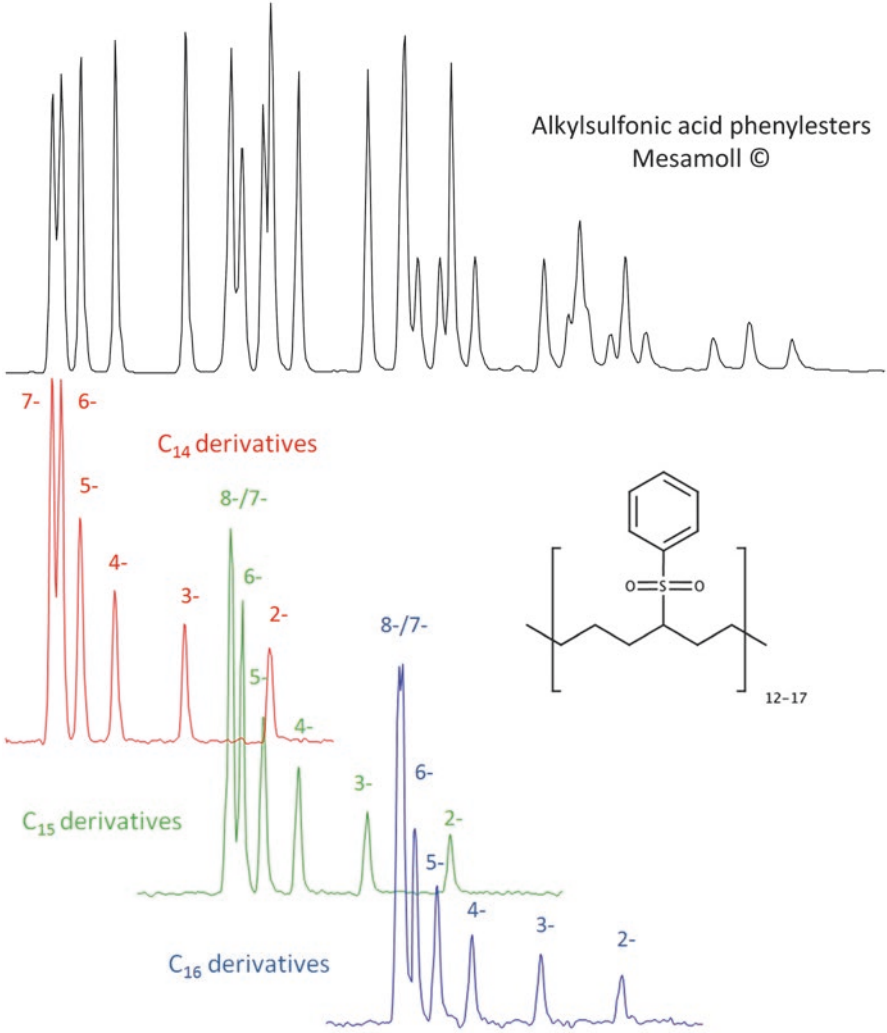


Fig. 2.58 Molecular structures and concentrations of TXIB and NBSS determined in two German rivers (Data adapted from Diskowitzky et al. 2004; Schwarzbauer and Heim 2005; Diskowitzky and Schwarzbauer 2015)

Alkylsulfonic acid phenyl esters (ASPEs, Mesamoll®) are alternatives for phthalate-based plasticizers but represent also all those plasticizers that have attracted less attention yet. Since ASPEs are substitutes for DEHP, they are accordingly constituents of PVC, polyurethanes and natural rubber. ASPEs are a group of homologues and isomers as depicted in Fig. 2.59. They have been detected in different environmental compartments also illustrated also in Fig. 2.59. Although the knowledge on the environmental fate and distribution of ASPE is very limited so far, these data point to a widespread occurrence.

A second group of technical agents are related partly to paper and paper industry. Photo initiators are essential for producing chemically and physically resistant paper coatings, e.g. food carton labels. Examples of such additives are Quantacure EPD and ITX (used in UV printing inks) or DMPA (conventional photo initiator e.g. in polymer films) presented in Fig. 2.60. Also TMDD is a known technical agent acting as surfactant in printing inks, cleaning products and adhesives. Lastly, di-*iso*-propylnaphthalenes (DIPNs) have been identified as technical agents intensively used in paper industry and paper products. DIPNs are also introduced to a minor extent as substitutes of PCBs e.g. as heat carriers.

Many of these compounds are ingredients of common products used in daily life and are emitted via discharge of paper, plastics and related products and subsequent leaching of the substances from these materials. Additionally, they are used in high amounts during production and for numerous technical production steps. Therefore,



Sample	Concentration range	References
River sediments	20 - 33000 ng/g	Franke et al. 1995
Indoor dust	<0.1 - 550 ng/g	Fromme et al. 2017

Fig. 2.59 Gas chromatographic elution pattern of alkylsulfonic acid phenyl esters (homologues with C₁₄ to C₁₆ and its substitution isomers from 8-/7- to 2- position) and some environmental data (sum of ASPE in river sediments and indoor dust)

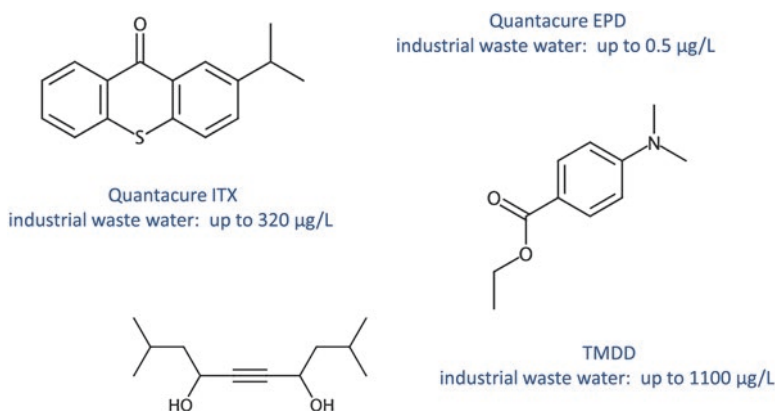


Fig. 2.60 Molecular structures and some environmental data of Quantacure EPD, Quantacure ITX, and TMDD (Data adapted from Dsikowitzky et al. 2015)

they are detected in both municipal sewage and industrial effluents. The elimination rate in sewage treatment plants is insufficient for many of these substances (e.g. for TMDD between 30% and 70%) and consequently, they are detected frequently in the aquatic environment. As an example, the linkage of the described substances to paper and paper industry is nicely reflected by the spatial distribution of DIPNs as representatives in sediments from the urban area of the Megacity Jakarta (see Fig. 2.61). Industrial point sources reflected by local concentration maxima are superimposed by a diffuse emission from paper waste all around the city.

General Note

Leaching or migration from materials like plastics or paper are a main emission source for technical additives. This is a more diffuse emission and, consequently, difficult to control and to manage.

The implications from such sediment contaminations by technical additives have been illustrated along the food chain at Jakarta Bay area. This area is subject to intensive fishing but also mussel farming. The bioaccumulation has been studied for DIPNs pointing to a significant uptake of these lipophilic substances by fishes and mussels in the range of 35–1300 ng/g dry weight (Dwiyitno et al. 2016).

Flame retardants are a last group exemplifying the pollution by technical additives. Some brominated representatives are already introduced in Sect. 2.1 (e.g. polybrominated diphenylesters). Further examples include phosphate derivatives such as **tris(2-chloroethyl) phosphate** TCEP or TCPP (two isomers of **tris(chloropropyl) phosphate**). Non-halogenated phosphates (such as **triethyl phosphate** TEP, **tributyl phosphates** TBP and **triphenyl phosphate** TPP) are also used as flame inhibitors in upholstered furniture, carpets, casings of electric devices etc. but more important as plastic additives (Fig. 2.62).

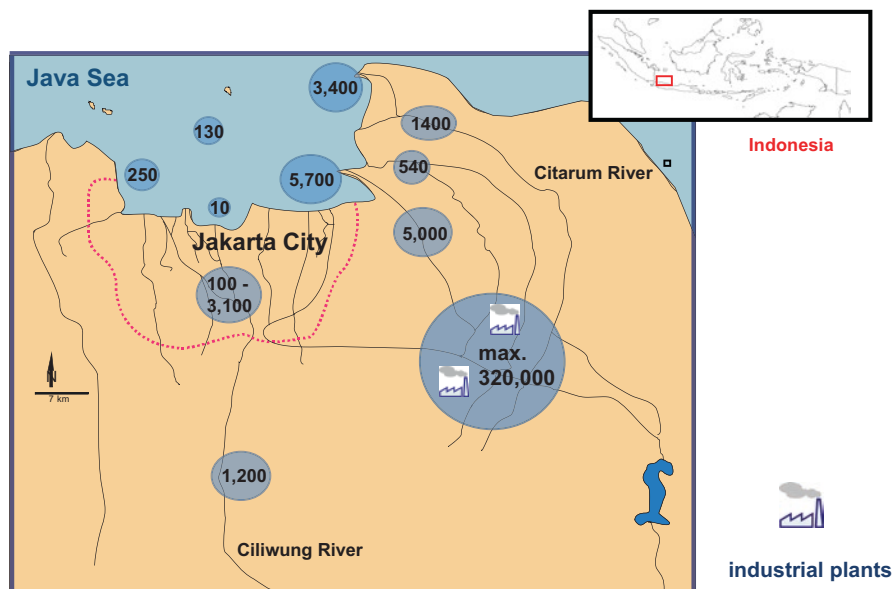


Fig. 2.61 Concentrations of DIPNs [ng/g] in surface sediments from the urban area and bay region of Jakarta, sampling October 2013 (unpublished results)

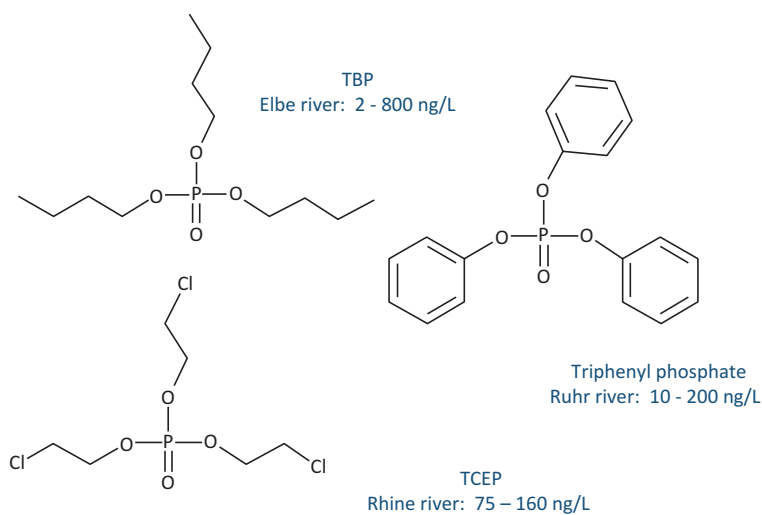


Fig. 2.62 Some phosphate based flame retardants with exemplifying environmental data (Data adapted from Bollman et al. 2011)

2.6 Explosives

Outlook

Explosives represent a specific pollution especially in soils. The chemical properties and the environmental fate of representative contaminants are described and discussed.

Keywords Nitro aromatics • TNT • Anaerobic metabolism • TAT • Picric acid

Military activities can lead to substantial emissions of pollutants to the environment. This applies not only for combat activities but also for many locations at which military acts in peace. Usage of ammunition on military bases, in particular careless handling and storage but also shooting, is a significant source for emissions of explosives to soil.

Most of the traditional but also of the more modern explosives exhibit a specific structural moiety, a multiple substitution with nitro groups. Some exemplifying molecular structures of typical explosives are given in Fig. 2.63. Well known explosives are TNT, nitroglycerin or RDX (main component of *C4*, *Composite Compound 4* or *Plastic Explosive 4*).

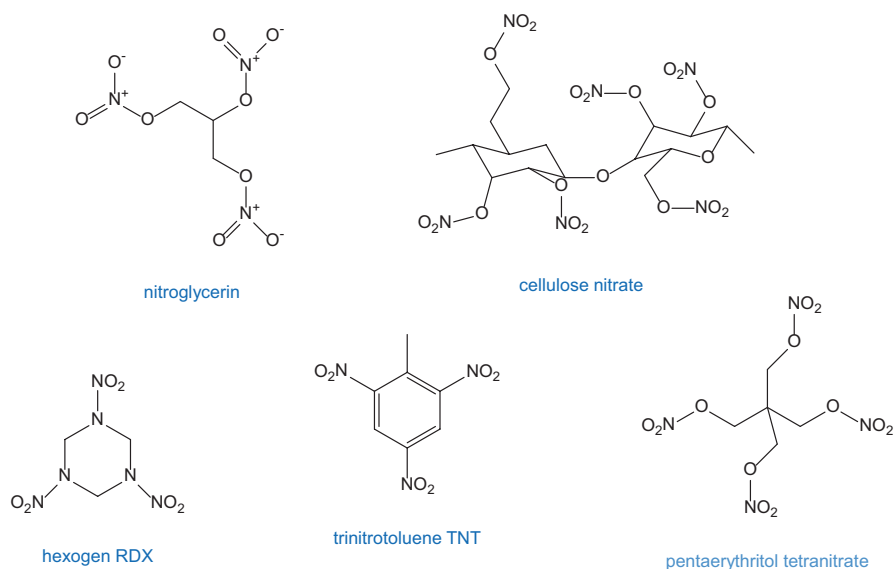


Fig. 2.63 Molecular structures of selected explosives

Excursion – How explosives are working

An explosion is related to a very abrupt release of energy in a very small volume. Explosions generate high temperatures and produce high pressure by generating high amounts of gases coupled with an enormous and fast expansion of the produced gases. Chemically triggered explosions are initiated by explosives that undergo a rapid oxidation. The kinetic of these oxidation reactions is highly controlled by the availability of oxygen. Oxygen-rich moieties support explosive reactions by delivering ‘intrinsic’ oxygen or oxidation potential. Nitro groups represent perfectly such oxygen-rich moieties and appear, consequently, in most explosives.

Table 2.15 Some relevant properties of TNT

Trinitrotoluene (TNT)	
Water solubility	130 mg/L (20 °C)
Vapour pressure	$1.5 \cdot 10^{-6}$ mbar (20 °C)
Velocity of detonation	6700–7000 m/s
Energy	1 kg TNT = 4,6 mega joule
(Eco)toxicology	Harmful for blood and liver, mutagenic, carcinogenic, phytotoxic

Although explosives tend to decompose they exhibit partly an astonishing high environmental stability. This has been documented in particular for soils and, hence, soil contamination by explosives on military bases is a tremendous problem. One main reason for this stability is related to the same property needed for being explosives, the high oxidation level of these compounds especially due to the multiple nitro substitution. The high oxidation level prevents in particular aromatic explosives like TNT from biotic mineralization under aerobic conditions.

The environmental fate in soil has been well studied for TNT. TNT has a slight water solubility, low vapor pressure and exhibits toxicological as well as ecotoxicological risk (see Table 2.15).

Main biotic transformation pathways include the reduction of the nitro groups to amino groups. In detail, hydrogenation by NADH results in two intermediates, with nitroso and hydroxyamino moieties. This reaction path is illustrated in Fig. 2.64.

Applying this reduction step to TNT transformation in soil all three nitro groups can be reduced but in a sequential way. Under aerobic conditions only an incomplete reduction of up to two nitro groups forming aminodinitrotoluene (ADNT) and diaminonitrotoluene (DANT) can be observed. ADNT is also the main metabolite in humans produced in the liver by nitroreductase. Anaerobic microbial degradation converts all nitro groups resulting in TAT, triaminotoluene. Noteworthy, the intermediates during nitro group reduction, containing nitrous and hydroxylamine moieties (see Fig. 2.65), are mainly responsible for main toxicological implications of TNT intake, e.g. mutagenic and carcinogenic effects (see also Lima et al. 2011).

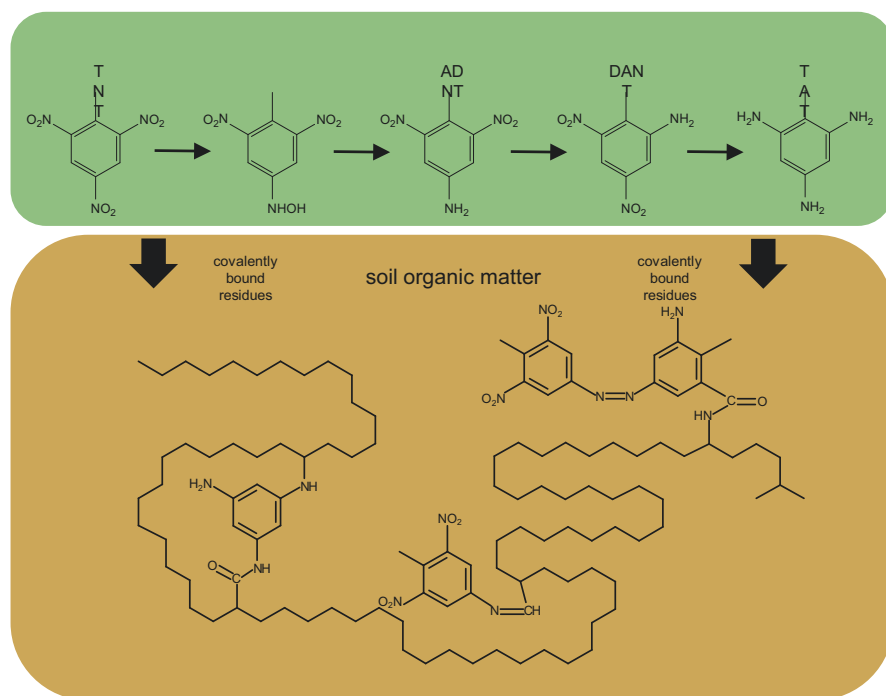


Fig. 2.66 Principal incorporation of TNT and its anaerobic metabolites into soil organic matter forming bound residues (Simplified after Reinecke and Schlömann 2007)

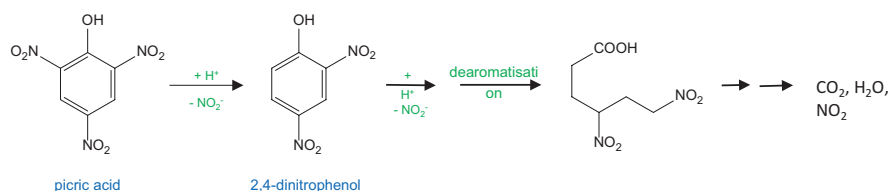


Fig. 2.67 Principal degradation pathway for picric acid (Simplified after Reinicke and Schlömann)

2.7 Aromatic Hydrocarbons – PAH and BTEX

Outlook

The group of aromatic hydrocarbons covers one ring as well as multiple ring systems. In the first group, the so-called BTEX compounds are the most relevant substances in terms of environmental interest. Further on, Polycyclic Aromatic Hydrocarbons (PAHs) represent a group of environmental relevant contaminants originated dominantly from two sources, petrogenic or pyrogenic emissions. Structural and environmental properties are described here.

Keywords Pyrogenic PAHs • Petrogenic PAHs • Source apportionment • Bay region • PAC

Benzene and its C_1 –/ C_2 -derivatives comprise an important group of environmental pollutants. Best known are the so-called BTEX substances covering benzene itself as well as toluene, ethylbenzene and the xylenes. Structures are given below (Fig. 2.68).

The polycyclic aromatic hydrocarbons, also called PAHs, have also received broad environmental interest for several decades. PAHs are not produced synthetically but appear in higher amounts in fossil matter, e.g. coals or petroleum, from which they are isolated for synthetic purposes. The environmental interest is related to toxic and ecotoxicological effects of some representatives, the different origins of PAHs, their distribution and dispersion and, as a result, their widely appearance in nature.

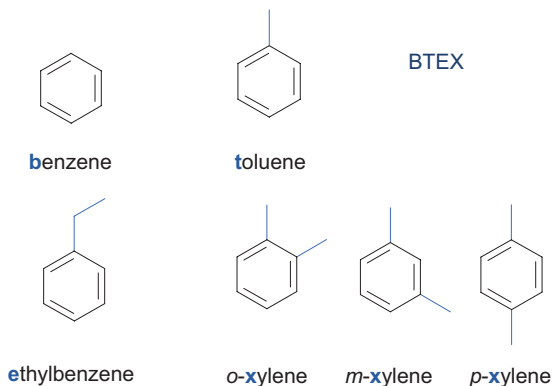
PAHs cover a large group of substances exhibiting a certain number of condensed aromatic rings. Ring multiplicity starts with two (naphthalene) but the maximum number of condensed rings is unlimited. Compounds with three and more rings can be arranged in different isomeric structures as the result of linear or angular condensation. Some representatives and the structural diversity of PAHs are illustrated in Fig. 2.69.

PAHs are measured in a wide variety of environmental compartments at different concentration levels. A very short summary is given in Table 2.16 illustrating the widespread occurrence of PAHs in the environment.

The ubiquitous occurrence of PAHs is strongly correlated with their emission sources. In principal, two different types can be differentiated: pyrogenic or petrogenic sources. Incomplete combustion of organic matter produces PAHs by two pathways. A de novo synthesis is known, where small and very reactive and unsaturated C_2 and C_4 moieties are formed in very hot pyrolysis or combustion regions (e.g. in the center of a flame). Transfer of these reactive particles to cooler areas (e.g. at the margin of the flame) leading to an incomplete combustion/pyrolysis, allows the particle to react by forming 6-ring cycles and, further on, condensed aromatic systems (see Fig. 2.70). The result of these processes is visible for example as the formation of soot, which consists of highly condensed aromatic polycyclic moieties.

A second pyrogenic pathway of PAH formation is the pyrogenic transformation of biogenic precursor molecules exhibiting already suitable ring systems. Steroids

Fig. 2.68 Molecular structures of the BTEX compounds



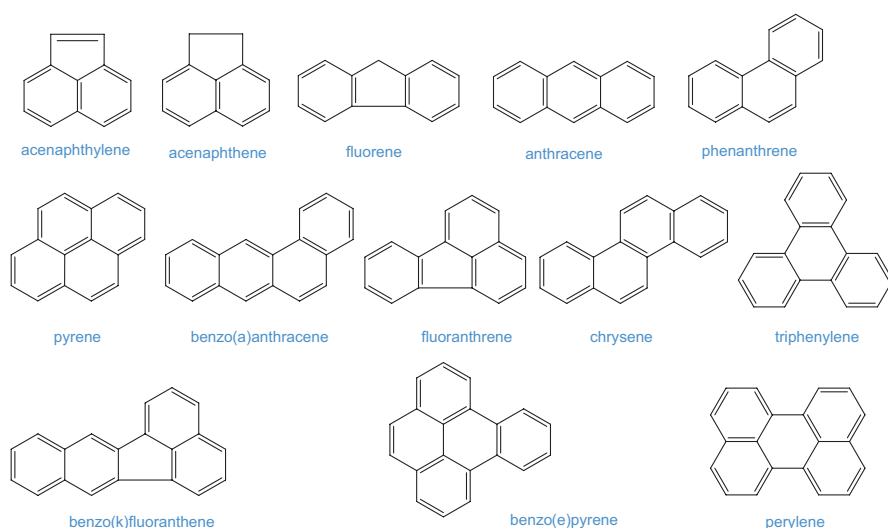


Fig. 2.69 Molecular structures of selected PAHs. Note the structural variations based on linear and angular condensation

Table 2.16 PAH concentrations measured in different environmental compartments

Sample	Concentration	Source
	$\sum PAH$	
Coastal sediments	25–1450 ng/g	Soclo et al. (2000)
Surface water	1000–9600 ng/g	Chen et al. (2004)
Surface sediments	130–7300 ng/g	Chen et al. (2004)
Painted comber (<i>serranus scriba</i>)	20–140 ng/g	Baumard et al. (1998)
Cigarette smoke	450–1200 ng/cigarette	Lian et al. (2015)
Tea	510–2750 ng/g	Londono et al. (2015)
Road dust	1–135 $\mu\text{g/g}$	Zheng et al. (2016)
	$\sum PAH 4$ (benzo[a]pyrene, benz[a]anthracene, chrysene and benzo[b]fluoranthene)	
Barbecued meat	0.1–195 ng/g	Duedahl-Olesen et al. (2015)

are such compounds with alicyclic ring systems that can react under pyrolytic condensations as illustrated in Fig. 2.71. Due to the defined structure of the precursor biomolecules the resulting PAHs are structural restricted to some specific and, therefore, indicative compounds such as chrysene.

The second main source for PAHs are fossil materials. PAHs are known to be formed by diagenetic and catagenetic processes from natural organic matter during thermal maturation (see Vol. 2 of this book series). For some defined biomolecules a clear diagenetic formation of specific compounds with polycyclic aromatic

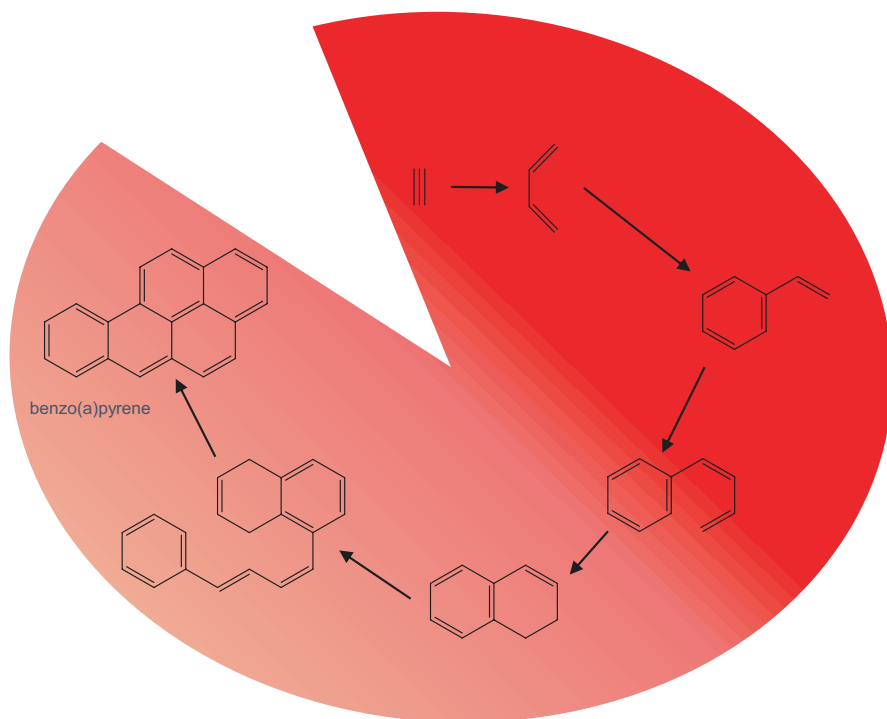


Fig. 2.70 Example for a de novo pyrogenic synthesis of PAHs. A decreasing temperature is illustrated by the color transition from red to light orange

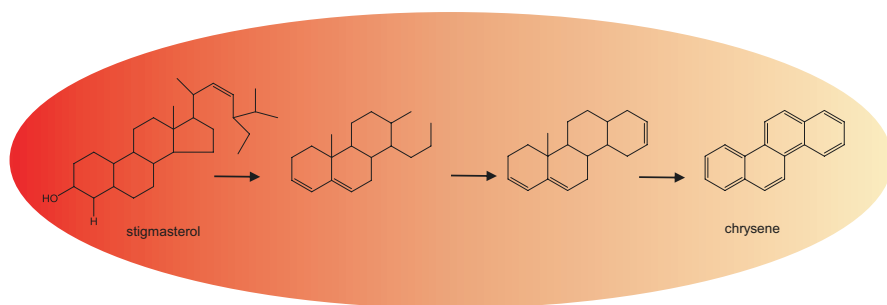


Fig. 2.71 Formation of chrysene from a steroid during incomplete combustion. A decreasing temperature is illustrated by the color transition from red to light orange

structures is described. As an example, the diagenetic and catagenetic formation of chrysene is depicted in Fig. 2.72. During diagenesis and catagenesis the biogenic steroid stigmasterol gets defunctionalized and the aliphatic four ring system is transformed to a condensed fully aromatic ring system, the chrysene. Noteworthy, beside the so-called parent PAHs (pure aromatic compounds) also the alkylated

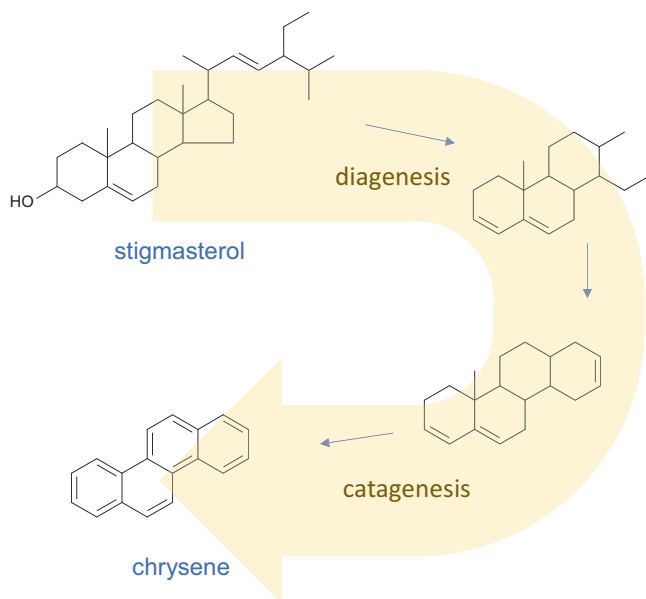


Fig. 2.72 Pathway of chrysene formation in fossil matter

Table 2.17 Relative thermodynamic stability of two PAH homologues

Compound	H_f (heat of formation) (kJ/mol)	ΔH_f relative to pyrene (kJ/mol)
Pyrene	125.2	0
Fluoranthene	190.2	65.0

derivatives (methylated compounds and higher homologues) are formed in higher abundances in fossil matter.

The different pathways of formation allow to use indicative PAH pattern to discriminate the corresponding origins. Generally, petrogenic and pyrogenic sources can be differentiated. Principal approach is the different thermodynamical stability of PAHs from both sources. Pyrogenic formation reveals a clear thermodynamically driven preference of individual PAH isomers, where the structures of petrogenic PAH are determined by the cyclic systems of the biogenic precursor molecules. Both structures often differ. As an example, the heat of formation as a parameter for thermodynamical stability differs for the both isomers pyrene and fluoranthene (see Table 2.17).

This difference induces a preferred formation of fluoranthene during pyrogenic genesis but a dominance of pyrene in fossil material. This can be expressed with the relative proportion of fluoranthene calculated as ratio of fluoranthene over the sum of fluoranthene and pyrene (see Table 2.18). Low values have been determined e.g. in crude oils or diesel fuel, whereas values above 0.5 have been measured from wood burning or similar processes (see Table 2.18).

Table 2.18 Indicative PAH ratios for petroleum and combustion samples

Source	$\frac{Fl}{Fl + Py}$	$\frac{C_0}{C_0 + C_1}$
Petroleum		
Diesel oil	0.26	0.18
Crude oil	0.23	–
Lubricating oil	0.29	0.35
Combustion of		
Lignite and brown coal	0.72	0.48
Wood	0.51	0.74
Gasoline	0.44	0.52
Bush fire	0.61	–

Mean values, adapted from Yunker et al. (2002)

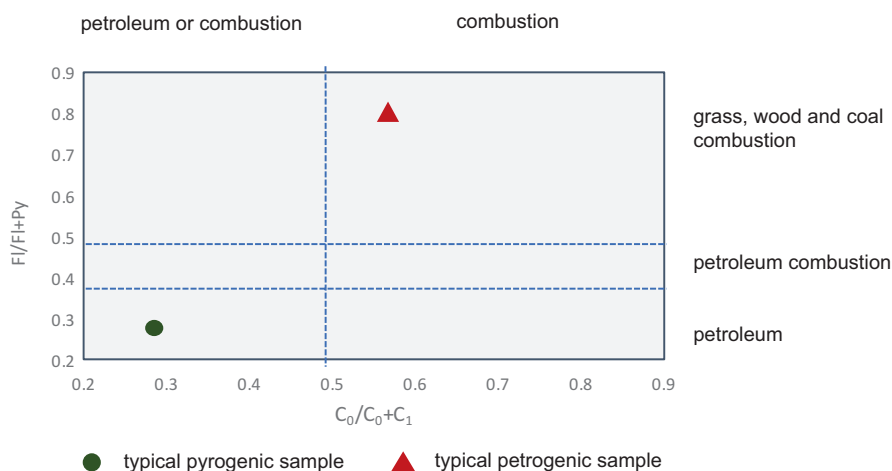


Fig. 2.73 Example for correlations of source specific PAH ratios according to Yunker et al. (2002)

A similar approach reveals ratios comparing the proportion of alkylated (mainly methylated) derivatives as compared to the unsubstituted PAHs. Here a preferential formation in fossil matter is evident leading to depleted PAH/(PAH + Me-PAH) values (see Table 2.18).

In order to enhance the sensitivity of such parameters, often a correlation of two parameters is used for an optimized emission source apportionment based on PAH ratios. An exemplifying scheme on how such approaches work is given in Fig. 2.73.

General Note

Their structural and physico-chemical variations allow a sources discrimination but the validity of the correlation is limited and needs to be checked for each sample material. Most indicative ratios are developed for aquatic sediments.

Aromatic hydrocarbons exhibit slightly higher polarity as compared to the aliphatic hydrocarbons leading to a higher water solubility. Within the PAHs the solubility decreases systematically with increasing ring numbers (see Fig. 2.74). Consequently, the higher PAHs are dominantly particle-associated pollutants, whereas BTEX and smaller PAH also appear as water contaminants.

With respect to (eco)toxicological effects a chronic toxicity is highly relevant for many PAH isomers. In particular carcinogenicity has been observed for several homologues or isomers. This harmful effect was able to be linked to some specific structural properties. These structural features have influence on the metabolism in higher organism. First transformation steps (as already introduced in Sect. 1.3) are the formation of dihydrols and subsequent activation prior to ring cleavage. This principal stepwise degradation of aromatic moieties in PAHs is illustrated for phenanthrene in Fig. 2.75. In more detail the initial reaction is an epoxidation at the aromatic ring and the following cleavage of this moiety forms the dihydrol. Normally, this cleavage reaction is relatively fast and the reactive epoxide exists for only a short period.

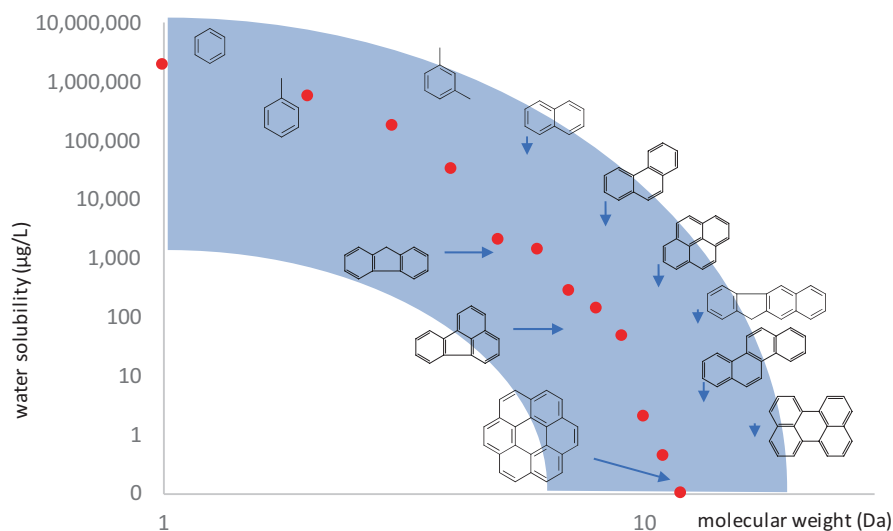


Fig. 2.74 Systematically decreasing water solubility of PAH with molecular weight. Please note the logarithm scale of both axis

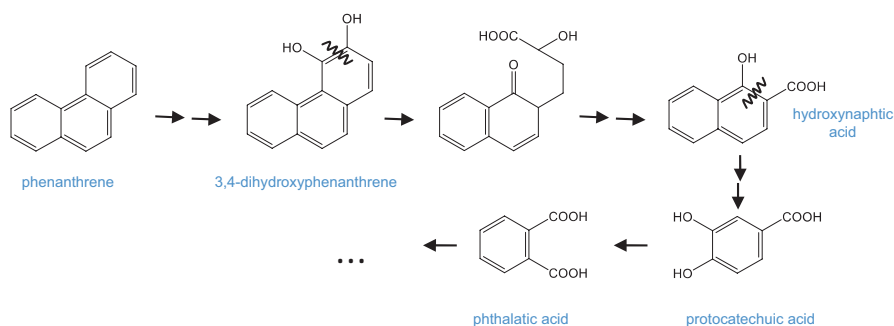


Fig. 2.75 One main degradation pathway of phenanthrene (Simplified after Reinecke and Schlömann 2007)

If a PAH exhibits a so-called *Bay Regions*, that means angular structures forming areas looking like bays (see Fig. 2.76), the formed epoxides are stabilized and exist in the organism for a prolonged time, in which they can react *inter alia* with the nitrogen-rich bases of DNA. This interaction can lead to the carcinogenic effects.

Especially the chronic toxicities lead to a relatively strict regulation of PAH contaminations leading to many threshold values in various compartments as summarized exemplarily in Table 2.19.

In addition to pure PAHs also compounds with oxygen, sulphur or nitrogen incorporated into the aromatic systems are known. Together with the PAHs they form the extended group of **polycyclic aromatic compounds**, PACs. Important representatives of N-, S- and O-PACs are depicted in Fig. 2.77. Noteworthy, here the hetero atoms N, S and O are part of the cyclic systems. Aromatic compounds substituted with functional groups (such as carboxylic, hydroxy or amino groups forming benzoic acid derivatives, phenols or anilines) do not belong to the PACs.

NSO-PACs appear associated with the PAHs. E.g., sulphur-containing benzo-thiophenes and nitrogen-containing carbazoles as well as their higher homologues are known as constituents in petroleum and coals. In addition, carbazoles have been analysed as pollutants from pyrogenic sources, e.g. in cigarette smoke. However, NSO-PACs are also widespread detected in environmental samples at various concentration levels as illustrated in Table 2.20.

The degradation pathways of PACs are a little bit more diverse as compared to PAHs but exhibit also many similarities. Beside the direct attack of the aromatic rings by insertion of hydroxyl groups for activating the ring system as a preliminary step for phenyl ring cleavage (see Fig. 2.78), also oxidation at or nearby the hetero atoms can be observed as initial degradation steps. Here, the oxidation also destabilizes the aromatic ring system enabling subsequent ring cleavage dominantly of the hetero atom containing ring. Some of these exemplifying degradation routes for sulphur-, nitrogen- and oxygen-containing PACs are given in Fig. 2.79.

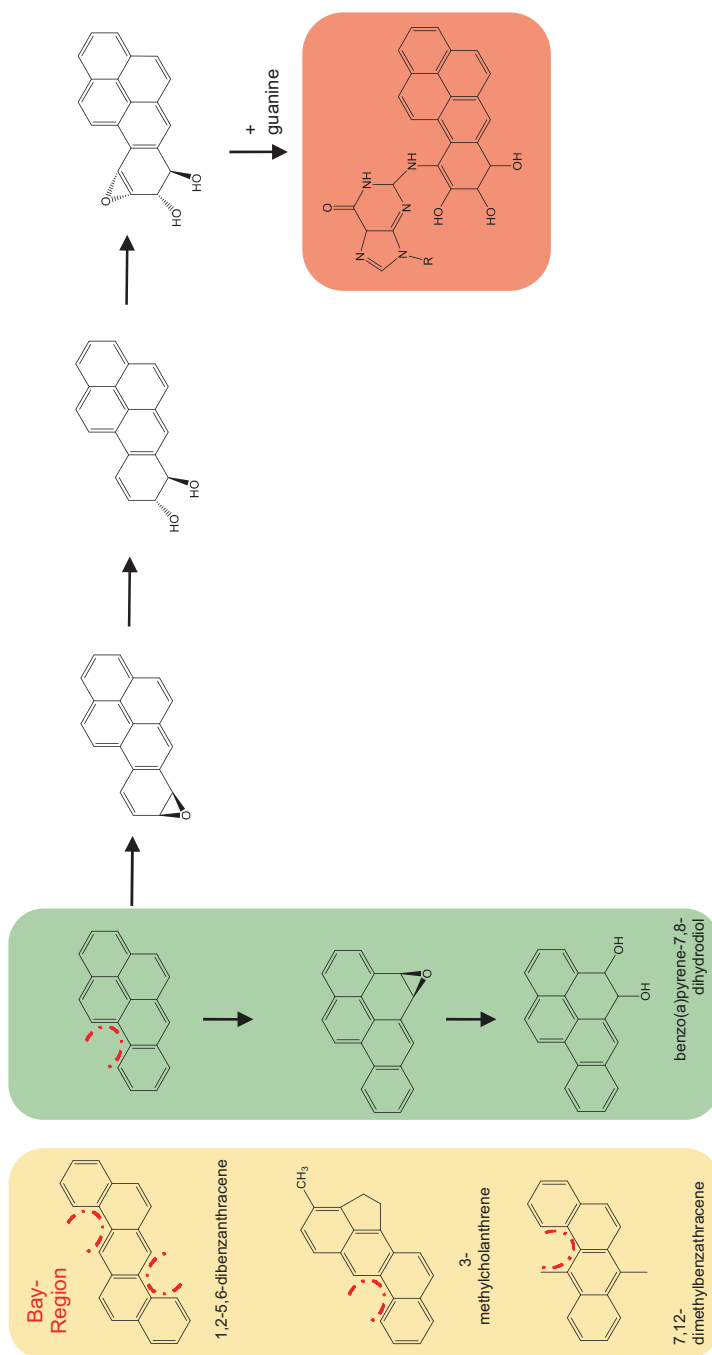


Fig. 2.76 Principles of the Bay-Region concept (Modified after Parlar and Angerhöfer 1995 and Reinecke and Schlömann 2007)

Table 2.19 Threshold values and regulations for some PAHs in various environmental media

Guidelines	Threshold value for PACs
European Council Directive on the quality of water intended for human consumption 1998	0.2 µg/l
WHO Guidelines for Drinking Water Quality 1984	0.01 µg/l (Benzo(a)pyrene)
European Council Directive concerning the quality required of surface water intended for the abstraction of drinking water in the Member States 1975	0.001 mg/l
Food Regulation for Meat	1 µg/kg meat product
Guidelines for soil remediation	1 mg/kg dry substance 0.0002 mg/l (as an eluate)

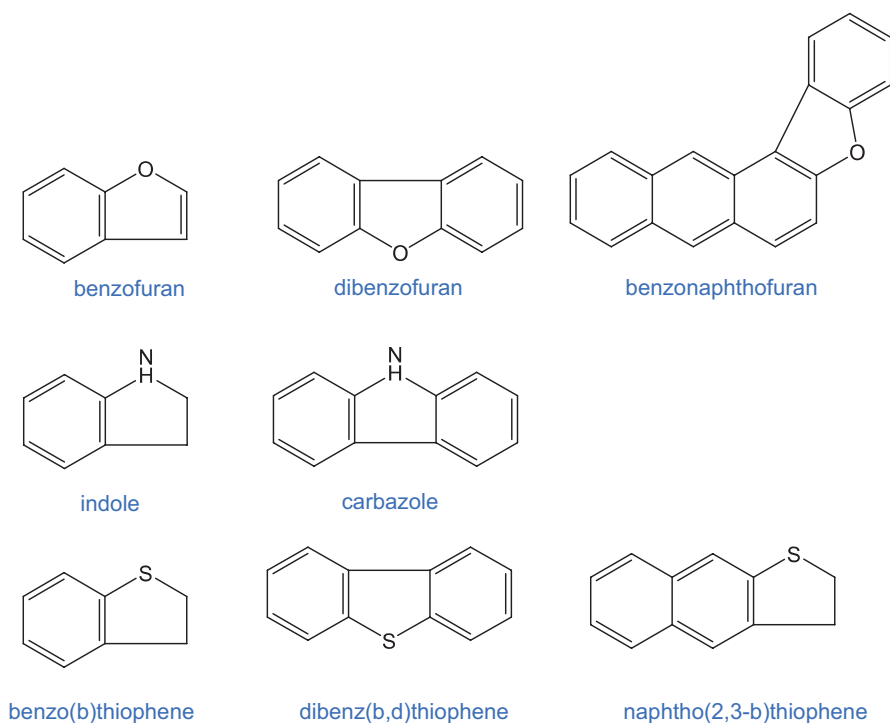
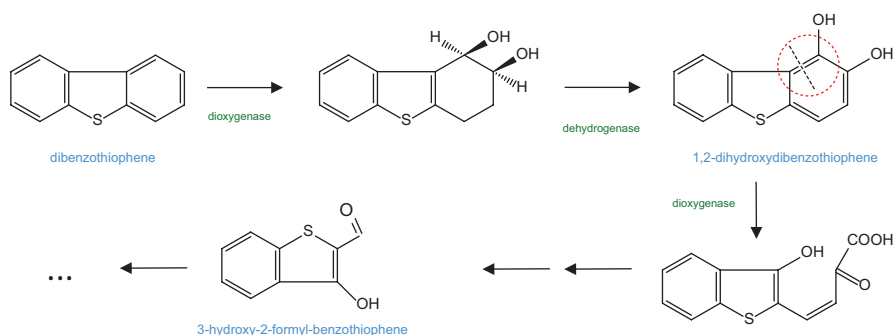
**Fig. 2.77** Molecular structures of selected oxygen-, nitrogen- and sulphur-containing PACs

Table 2.20 Some environmental concentrations of NSO-PACs

Compound	Concentration	Sample type	References
Acridine	2.3 µg/L	groundwater	Zamfirescu and Gratwohl (2001)
Benzothiophene	1.4–2.5 ng/L	river water	Götz et al. (1998)
Benzothiophene	0.01–1.36 mg/L	groundwater	Goerlitz et al. (1985)
Carbazole	1–65 ng/g	soil	Guo et al. (2014)
Dibenzofuran	11–32 ng/kg	marine sediment	Broman et al. (1991)
Dibenzofuran	1–56 ng/L	tap water	Shiraishi et al. (1985)
Dibenzofuran	0.03–0.2 ng/L	lake water	Shiraishi et al. (1985)
Methylbenzofuran	54.2 µg/L	groundwater	Zamfirescu and Gratwohl (2001)
Thiophene	6.7 g/kg	<i>Tagetes Lucida</i> (flower)	Marotti et al. (2010)
Thioxanthene	3 µg/L	groundwater	Zamfirescu and Gratwohl (2001)
Xanthene	4.8 µg/L	groundwater	Zamfirescu and Gratwohl (2001)

**Fig. 2.78** Example for initial steps of a microbial transformation pathway of a sulphur-containing PAC with ring cleavage at the phenyl moiety (Simplified after Reinecke and Schlömann 2007)

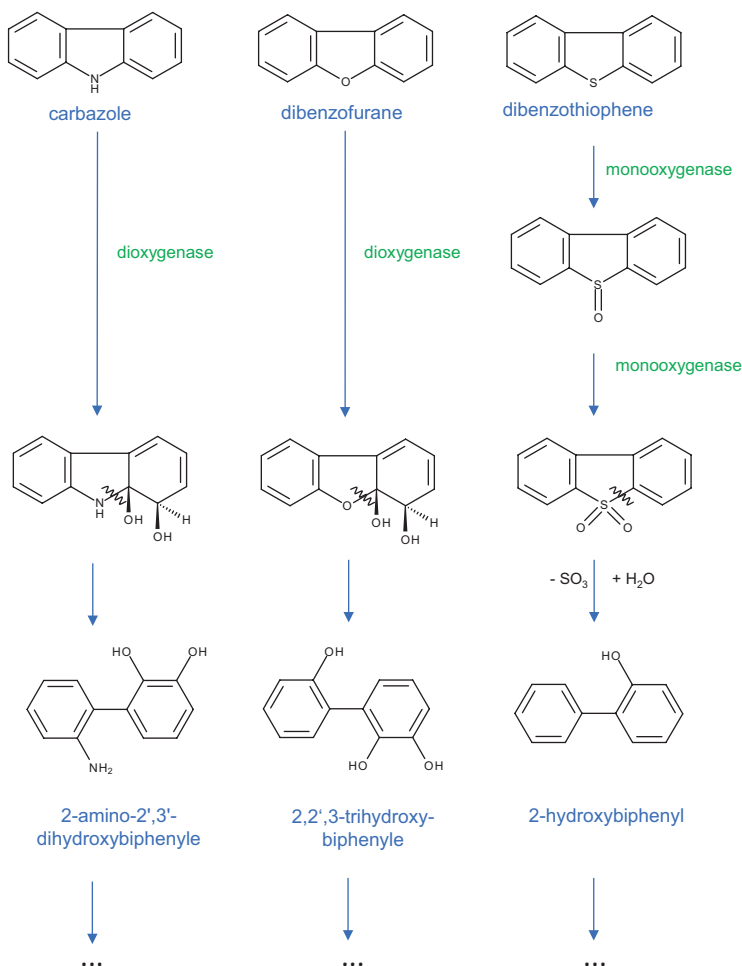


Fig. 2.79 Principal biotic degradation pathways of representative N,S,O-PACs (Simplified after Reinecke and Schlömann 2007)

2.8 Organometallics

Outlook

Several compounds, in which organic moieties are covalently bound to metals, are known as environmental pollutants. Here, microbially formed methyl mercury species and synthetic butyl tin compounds are introduced and their environmental fate and impact are discussed.

Keywords Biomethylation • Mercury • Tin • Technical usage • Homologue pattern

Inorganic and organic chemistry are not strictly separated. Compounds exhibiting both organic moieties and metals are well known not only in synthesis chemistry but also as natural substances. Beside organic salts, in which metals and organic moieties are linked via ionic bonds (e.g. sodium oleate or butyl lithium), a group of compounds exists with covalent bonds between metal atoms and organic carbon atoms, the so-called organometallic compounds or organometallics. Two representative examples are given in Fig. 2.80.

Covalent bonds to organic carbon are known for most metals. The stability of organometallics depends on the nature of both metal and organic moieties (e.g. aliphatic or aromatic moieties, carbonyls etc.). Nearly all transition metals as well as some alkaline earth metals are known to form covalent bonds to organic moieties, whereas alkali metals just build up organic salts. Examples for common metals in organometallics are iron (e.g. ferrocene Ph_2Fe), lead (e.g. tetraethyl lead as anti-knock additive) or magnesia (e.g. Grignard reagents with a principal composition RMgX with R = aliphatic or aromatic moiety and X = halogen). From an environmental point of view only those organometallics are relevant that are produced in higher quantities, discharged to the environment and exhibit a high stability under

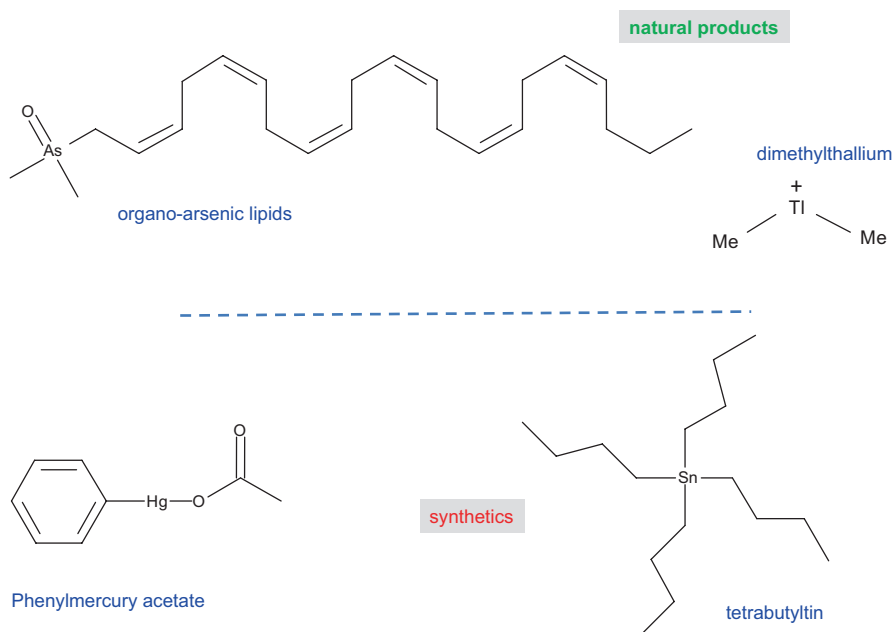


Fig. 2.80 Molecular structures of four organometallic compounds. The arsenic-organic compound occurs naturally as lipid in some fish species. Dimethyl thallium results from natural microbial biomethylation of thallium ions. On the contrary, phenyl mercury acetate is one of the first synthetic pesticides (usage started in Germany in 1913) and tetrabutyl tin is a common synthetic precursor in technical butyl tin chemistry

I		II												III	IV	V	VI	VII	VIII			
1 H																			2 He			
3 Li	4 Be	covalent bonds, multiple center bonds										5 B	6 C	7 N	8 O	9 F	10 Ne					
11 Na	12 Mg	transition metals										13 Al	14 Si	15 P	16 S	17 Cl	18 Ar					
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr					
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe					
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn					
87 Fr	88 Ra	89 Ac											covalent bonds									
ion bonds																						

Fig. 2.81 Mode of organometallic bonds linked with the PSE location of the metals (Modified after Elschenbroich and Salzer 1990). Metals marked in red are known to form environmental relevant organometallics

natural conditions. Therefore, only a few substance groups are known as environmental pollutants yet. The metals forming such environmental stable substances (e.g. Hg, Tl, Pb or As) appear mainly in the lower right of the period table of the elements (see Fig. 2.81).

Principally, two different pathways of formation exist for anthropogenic organometallics. Either anthropogenically released metals are linked to organic moieties via biotic (in particular microbial) processes or technical synthesized organometallics are released to the environment as the result of production or usage. In the following two representative groups of organometallics harming the environment are discussed.

2.8.1 Methylated Mercury Species

The appearance of organomercury compounds as environmental pollutants is highly related to a catastrophe of the 50s, the Minimata disaster. An uncontrolled discharge of industrial sewage containing high amounts of methyl mercury led finally to a bioaccumulation of this special mercury species in humans harming more than 10.000 persons. Methylation of mercury produces first an ionic species, the monomethyl mercury, which exhibit tremendous different properties as compared to inorganic mercury e.g. in salts like vermilion (HgS). For an environmental assessment the higher water solubility and the corresponding enhanced mobility as well as the

Table 2.21 Physico-chemical and corresponding environmental properties of mercury and its methylated derivatives

Compound	Characteristic
HgS	Insoluble
CH_3Hg^+	Hydrophilic
$(\text{CH}_3)_2\text{Hg}$	Lipophilic and volatile

Modified after Bliefert (2002)

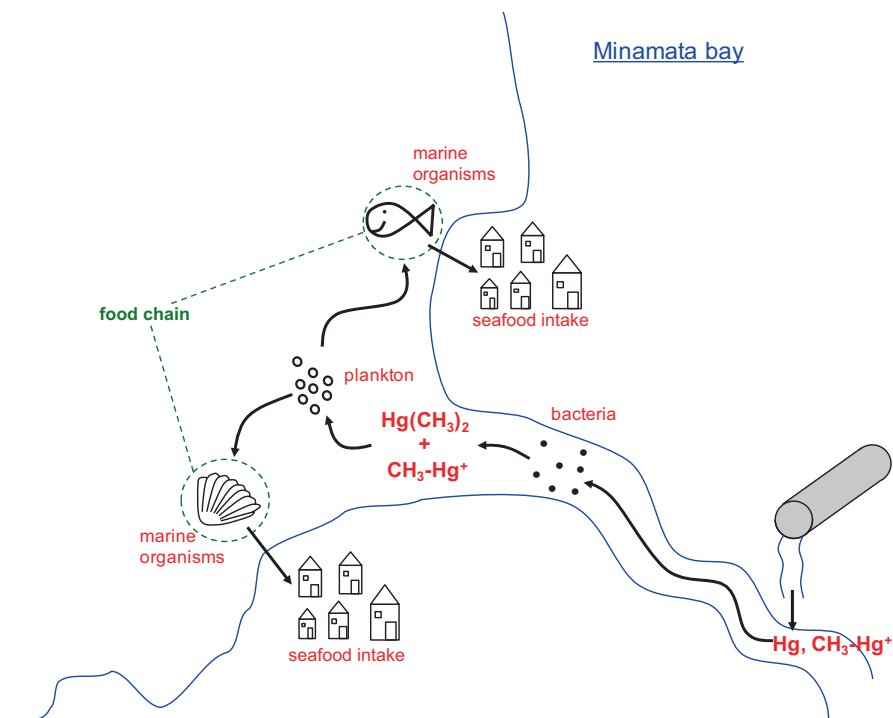


Fig. 2.82 A schematic illustration of the organo-mercury pathway resulting in the Minamata disaster

elevated bioaccumulation potential are the most important characteristics of mono-methyl mercury. A second methylation forming dimethyl mercury changes once more the physico-chemical properties, the non-ionic species are lipophilic and exhibit consequently a lower water solubility but higher volatility as well as a high tendency to accumulate in organism. All these changes are summarized in Table 2.21.

The specific properties of methylated mercury, as the result of linking organic moieties to this metal, was responsible for the extent and nature of the minimata poisoning. A high mobility in the water phase and the corresponding fast dispersion, the high bioaccumulation rate within the food chain and the uptake by residents via seafood consumption as well as the elevated toxicity of the methylated derivatives effected this disaster (see. Fig. 2.82).

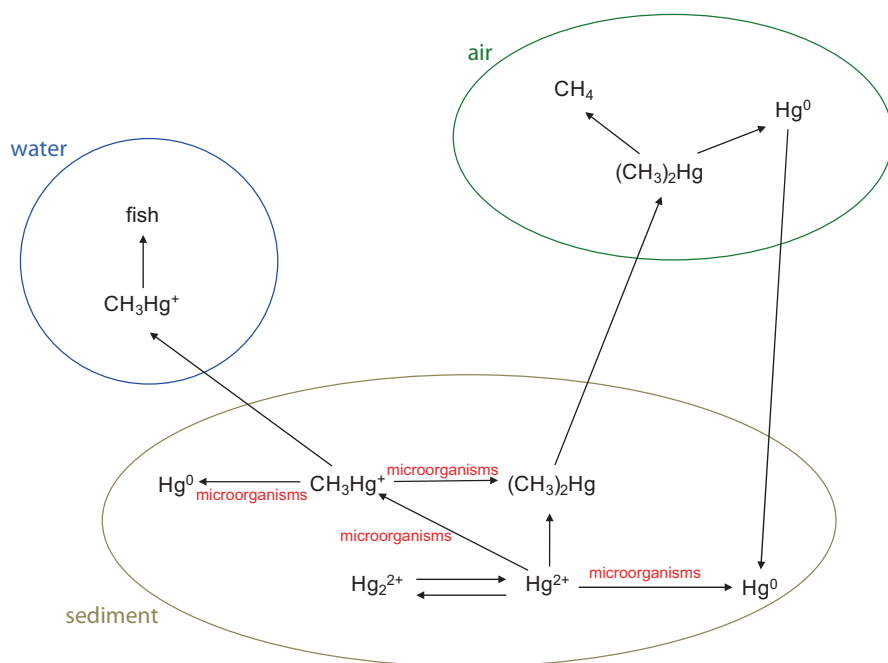


Fig. 2.83 Environmental dispersion and transformation of mercury and its methylated derivatives in the aquatic environment and adjacent compartments (Modified after O'Neill 1998; Bliefert 2002; Reinecke and Schlömann 2007; Fent 2013)

Noteworthy, methylation of mercury is also a natural process. In particular, microbial assisted biomethylation has been observed in the aquatic environment. Preferred location for such processes are the anaerobic sediments, in which both mono- and dimethylated mercury species are formed. This anaerobic biomethylation appears at all locations polluted with mercury, e.g. at burdens of technical chloralkali processes. A principal scheme on how methyl mercury species are formed and distributed in the aquatic environment according to their physico-chemical properties is given in Fig. 2.83.

Examples for methyl mercury concentrations and amounts detected in the aquatic environment are summarized exemplarily in Table 2.22.

Table 2.22 Some exemplifying quantitative data of methyl mercury species in the aquatic environment

Environmental compartment	Species	Study area	Concentration [ng/g dry]	References
Methylmercury				
Sediment	–	Baltimore Harbor, Maryland, USA	0.05–1.28	Mason and Lawrence (1999)
		Groot Buitenschoor, Scheldt estuary, Belgium	0.8–5.7	Muhaya et al. (1997)
		Florida Bay, South Florida Estuaries, USA	0.001–0.318	Kannan et al. (1998)
Biota	Clams	Baltimore Harbor, Maryland, USA	0.36–7.52	Mason and Lawrence (1999)
	Nereis diversicolor	Groot Buitenschoor, Scheldt estuary, Belgium	3.1–34.4	Muhaya et al. (1997)
	Isopods	Baltimore Harbor, Maryland, USA	30.0–65.0	Mason and Lawrence (1999)
	Hardhead catfish	Florida Bay, South Florida Estuaries, USA	1400–1800	Kannan et al. (1998)
Dimethylmercury				
Sediment	–	marine sediment core Kaštela Bay, Croatia	0.003–0.15	Kwokai et al. (2002)
		Sediment core from Sepetiba Bay, Brazil	43–278	Quevauviller et al. (1992)

2.8.2 Butyl Tin Compounds

The second group of environmentally relevant organometallics presented here belongs to the group of alkyl and aryl tin species. In principal, tin has the potential to be linked covalently with a maximum of four substituents. Organotin compounds are known with one to four either alkyl or aryl substituents. Most prominent species are phenyl, octyl, butyl and methyl tin compounds. These compounds are synthetically produced (with partial exception for methylated species, that are also known to be formed via biomethylation) and represent highly specific technical agents. Due to their dominant technical and environmental relevance, the following discussion will focus on the butyl tin compounds.

From a structural point of view the most important characteristic for the butyl tin compounds is the degree of substitution. Monobutyl, dibutyl and tributyl tin compounds are ionic species, whereas the fully substituted tetrabutyl tin is a nonionic molecule (see Fig. 2.84). The three cations are characterized by an enhanced water solubility, whereas tetrabutyl tin is a very lipophilic compound, e.g. highly soluble in hexane. These properties have an important implication for the environmental dispersion of butyl tin compounds.

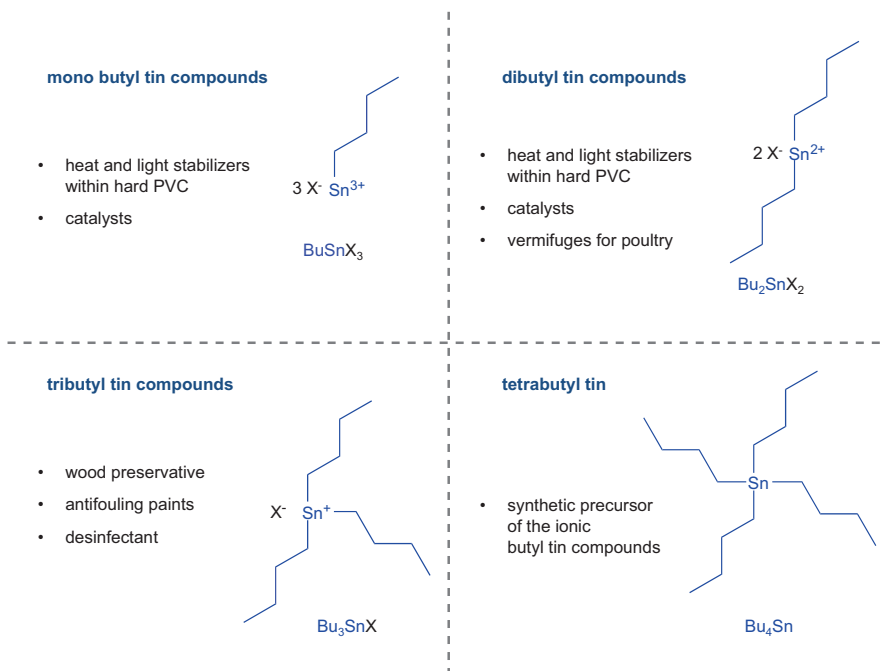


Fig. 2.84 Molecular structures and technical applications of the four most prominent butyl tin species (Modified after Blunden and Chapman 1986 and Jantzen 1992)

The non-polar tetraalkylated species appear dominantly adsorbed on particles, in particular in aquatic sediments and corresponding suspended particulate matter. For the ionic derivatives, an occurrence in both dissolved in water but also adsorbed on particles can be observed. Additionally, biota take up butyl tin compounds to a considerable extent. Here a more complex dispersion especially within the aquatic environment is evident. Figure 2.85 illustrates the distribution of ionic butyl tin species within the different compartments in the hydrosphere including typical quantitative contamination levels.

Not only the degree of alkylation but also the type of substituents determines the (eco)toxic properties of butyl tin compounds. It is known, that different substituents provoke toxicity for different species. An overview of this specificity is given in Fig. 2.86. As an example, methylated tin compounds exhibit highest toxicity for insects, whereas the most abundant butyl tin species are most toxic for fishes, mussels, or fungi. Noteworthy, the comparison of butenyl and butyl tin compounds demonstrates the partly high specificity of substituents. The unsaturated substitution produces toxicity mainly for gram negative bacteria, but saturated butyl tin compounds are toxic for gram positive bacteria.

For assessing the (eco)toxicity of organotin compounds some rules of thumb exist as summarized in Fig. 2.87.

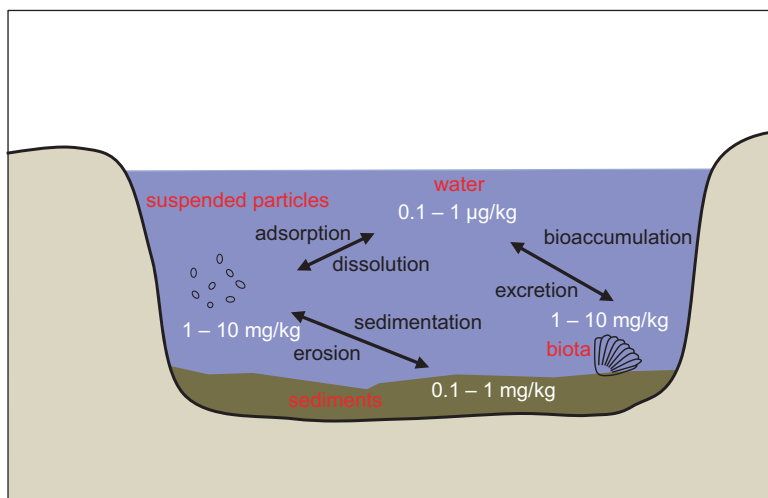


Fig. 2.85 Representative concentration ranges of butyl tin compounds in various compartments of the hydrosphere (harbour area) reflecting the wider distribution of these contaminants (Adapted from and modified after Fent 2013)

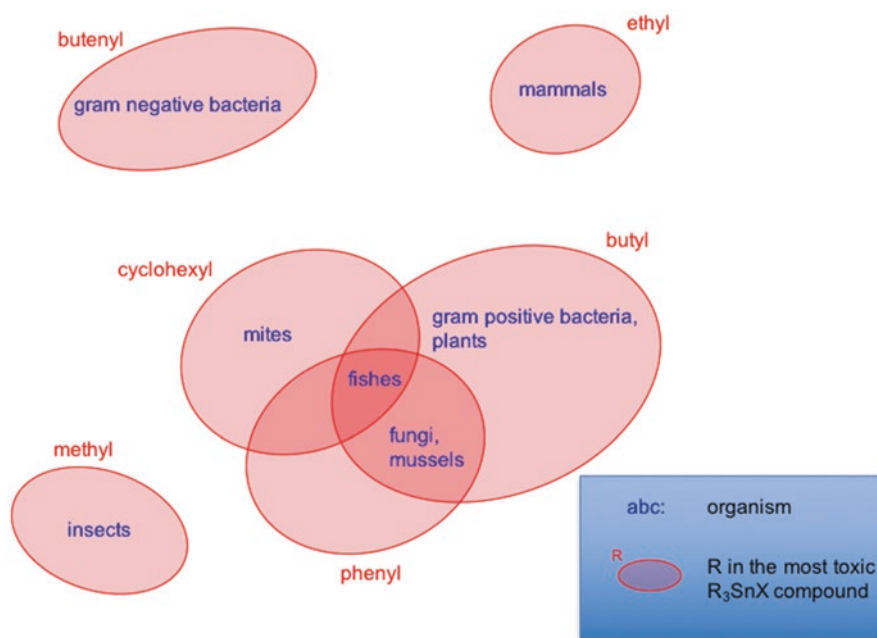


Fig. 2.86 Specificity of tin organic substituents for the toxicity on individual groups of organisms (Modified after Craig 1986 and Jantzen 1992)

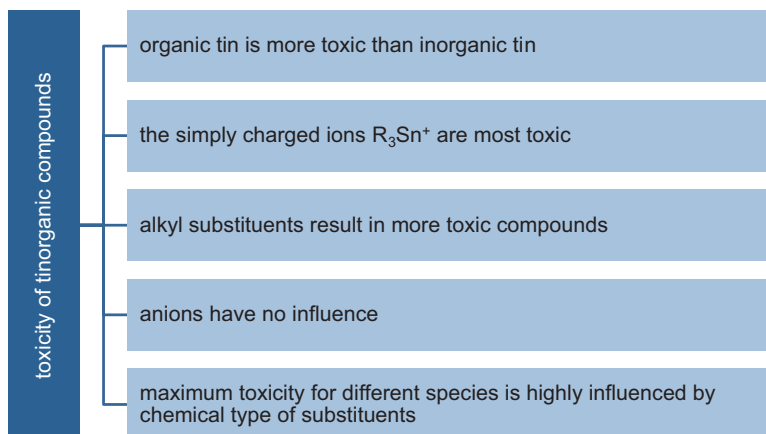


Fig. 2.87 Relevant aspects characterizing the toxicity of organotin compounds

Lastly, also the technical applications as well as the corresponding emission pathways of butyl tin compounds differ related to the degree of substitution. Mono and dibutyl tin are mainly used as additives in PVC and related polymers preventing aging due to light or heat. Further on, these compounds are used as catalysts in some technical reactions (e.g. poly urethane synthesis). More specifically, dibutyl tin is used as vermifuges in poultry farming. On the contrary, tributyl tin has been widely used as active ingredient in antifouling paints especially for boat hulls. In principal, two different modes of functioning are known for maritime antifouling paints. A first generation of paintings released the active ingredients, here tributyl tin, by direct migration/desorption from the painting films, which points to diffusion within the films as dominant process regulating the leaching rate. In more modern paintings the active component is embedded and fixed in a polymer film. Here, the abrasion of the film due to shearing forces during shipping regulates the leaching with a more constant rate (see Fig. 2.88).

However, it has to be noted that its application as antifouling agent implies a considerable emission of tributyl tin towards the aquatic environment. The corresponding toxic effects for aquatic organisms are exemplified in Table 2.23.

For tetrabutyl tin a direct technical application is not known. However, tetrabutyl tin is the main precursor for technical synthesis of all ionic butyl tin compounds. Reaction of tetrabutyl tin and tin tetrachloride results in butyl tin species, where the ratio of both educts determines the degree of alkylation of the product as figured out in Fig. 2.89.

For the aquatic environment, dominant pathways are summarized in Fig. 2.85. Mono- and dibutyl tin represent mainly municipal sewage effluents due to leaching of these compounds from plastics and subsequent insufficient removal in sewage treatment plants. Tributyl tin results from its application as antifouling paints and represents emissions from shipping activities. Finally, the occurrence of tetrabutyl

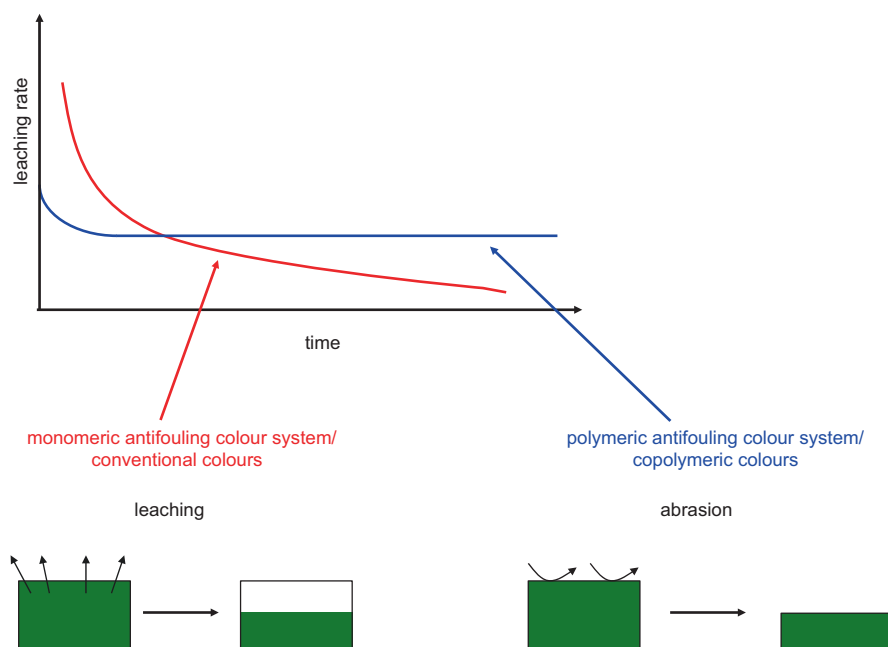


Fig. 2.88 Long term behavior and mode of dispersion of two different types of antifouling paints (Adapted from and modified after Jantzen 1992 and references cited therein)

Table 2.23 Ecotoxicological data of tributyl tin related to individual organisms

Organism	Ecotoxicological parameter	Concentration [$\mu\text{g/L}$]
Guppy	7d-LC ₅₀	16.0
Oyster	growth stop	0.3
	reduced growth	0.004
Shrimps (old)	96 h-LC ₅₀	0.7
Shrimps (young)	96 h-LC ₅₀	0.3
Salmon	6 h-LC ₅₀	11.0
	12 h-LC ₅₀	4.0
	96 h-LC ₅₀	0.3

According to Jantzen (1992) and references cited therein

tin can only be assigned to industrial emissions from technical butyl tin syntheses. These different emission pathways into the aquatic environment are also reflected by quantitative data from specific samples, e.g. sewage effluents or harbor locations as pointed out in Fig. 2.90.

Using these indicative properties, a differentiation of the corresponding emission sources is feasible. To some extent disproportionation processes have to be considered, which have been observed in particular in sediments (see. Fig. 2.91).

However, these reactions shifting the relative distribution of butyl tin compounds seem to have only a minor impact. This can be nicely demonstrated by butyl tin

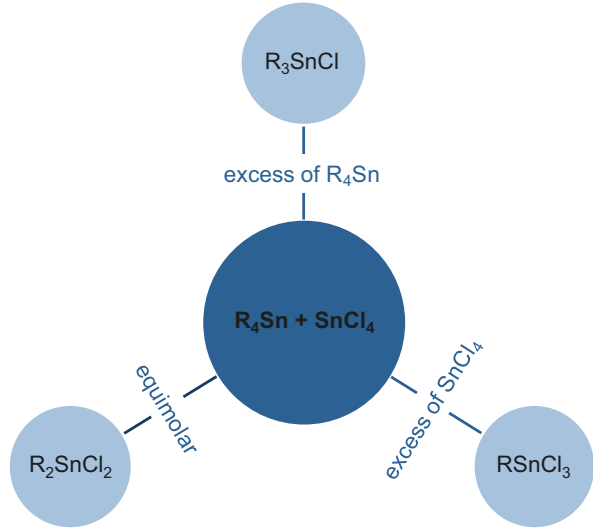


Fig. 2.89 Principal technical synthesis of butyl tin compounds

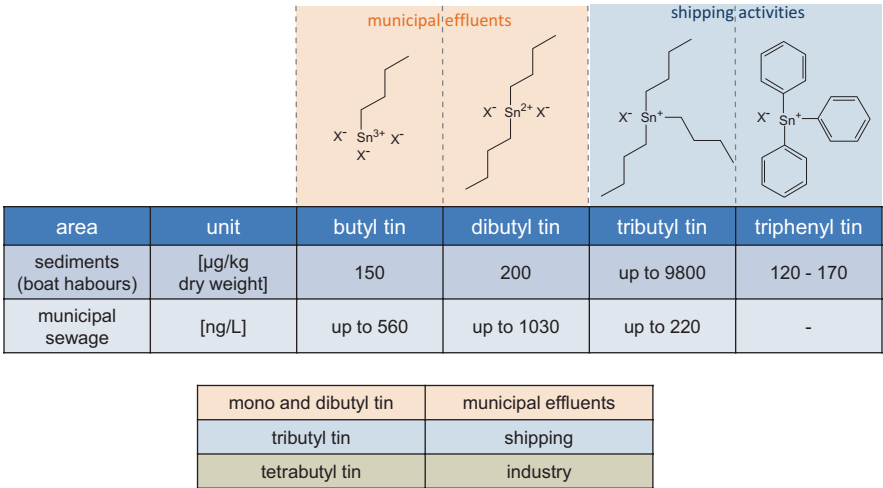


Fig. 2.90 Occurrence of different butyl tin species as the result of different emission sources. The source specificity of the degree of butylation is summarized in the table (Data adapted from Fent 2013)

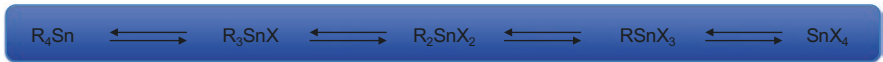


Fig. 2.91 Disproportionation of butyl tin compounds

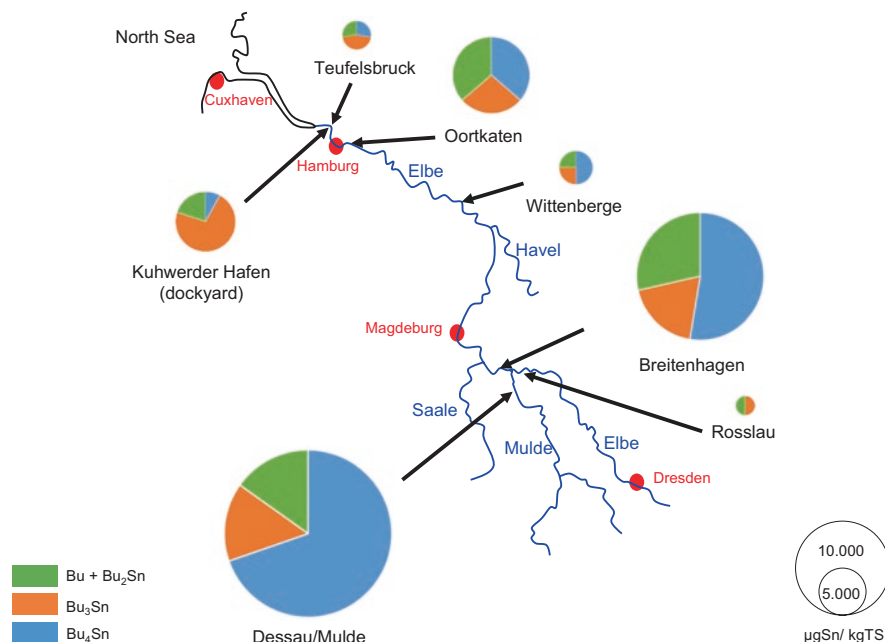


Fig. 2.92 Pattern of butyl tin compounds along the Elbe river longitudinal profile as influenced by different emission sources (Adapted and simplified after Jantzen et al. 1993)

analyses performed on sediments from the Elbe river as illustrated in Fig. 2.92. Mono- to tetrabutyl tin compounds have been analysed in the river course from the German/Czech border to the river mouth at the German Bight. For mono- and dibutyl tin a varying contribution along the total river profile is observable reflecting the varying municipal sewage water emissions. Tetrabutyl tin occurred firstly at the tributary Mulde River. Here, point source emissions from a local industry synthesizing butyl tin compounds is evident and visible till the North Sea. Finally, tributyl tin was observed in all sediment samples reflecting the common shipping activities on the river, but in one Hamburg harbor sediment a local concentration maximum was observed linked to a dockyard, in which antifouling paints have been handled on a high scale.

General Note

The environmental characterization of butyl tin compounds is dominated by the degree of substitution. Whether one, two, three or four substituents are linked to tin,

- influences their toxicity
- determines their environmental dispersion and accumulation
- differentiates their technical applications and
- also their emission pathways

Excursion – Butyl tin compounds in mass spectrometry

Although a metal is incorporated in the molecular structure, some butyl tin species are perfectly detectable in GC/MS analyses. In particular, the unique isotope pattern of tin is perfectly visible in the mass spectra (see below). The hindrance for analyzing ionic species (mono- to trisubstituted compounds) related to their low volatility and consequently inappropriateness for GC separation, can be overcome by derivatization approaches, e.g. using potassium tetraethyl borate. This derivatization produces peralkylated species that can be easily analysed by GC/MS. The mass spectra of such a derivatized substance (formerly tributyl tin, now ethylated to tributylethyl tin) is given below.

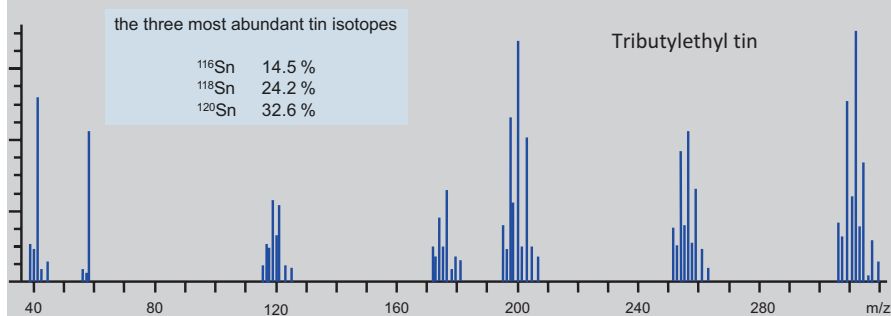


Figure: Mass spectrum of a peralkylated tin compound with its characteristic tin isotope pattern

References

- Alloway BJ, Ayres DC (1996) *Schadstoffe in der Umwelt*. Spektrum Akademischer Verlag, Heidelberg
- Amweg EL, Weston DP, Ureda NM (2005) Use and toxicity of pyrethroid pesticides in the Central Valley, California, USA. *Environ Tox Chem* 24:966–972
- Andreozzi R, Raffaele M, Nicklas P (2003) Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment. *Chemosphere* 50:1319–1330
- Ballschmitter K (2003) Pattern and sources of naturally produced organohalogens in the marine environment: biogenic formation of organohalogens. *Chemosphere* 52:313–324
- Ballschmitter K, Bacher R (1996) *Dioxine*. Weinheim, VCH
- Baumard P, Budzinski H, Garrigues P, Sorbe JC, Burgeot T, Bellocq J (1998) Concentrations of PAHs (Polycyclic Aromatic Hydrocarbons) in various marine organisms in relation to those in sediments and to trophic level. *Mar Pollut Bull* 36:951–960
- Benotti MJ, Trenholm RA, Vanderford BJ, Holaday JC, Stanford BD, Snyder SA (2009) Pharmaceuticals and endocrine disrupting compounds in U.S. drinking water. *Environ Sci Technol* 43:597–603
- Berger M, Schwarzbauer J (2016) Historical deposition of riverine contamination on terrestrial floodplains as revealed by organic indicators from an industrial point source. *Wat Air Soil Pollut* 227:20

- Bester K (2005) Polycyclic musks in the Ruhr catchment area—transport, discharges of waste water, and transformations of HHCb, AHTN and HHCb-lactone. *J Environ Monitoring* 7:43–51
- Björklund JA, Thuresson K, de Wit C (2009) Perfluoroalkyl compounds (PFCs) in indoor dust: concentrations, human exposure estimates, and sources. *Environ Sci Technol* 43:2276–2281
- Bliefert C (2002) *Umweltchemie*, 3rd edn. Weinheim, Wiley VCH
- Blunden SJ, Chapman A (1986) Organotin compounds in the environment. In: Craig PF (ed) *Organometallic compounds in the environment*. Longman, Harlow, pp 111–159
- Bollman U, Möller A, Xie Z, Ebinghaus R, Einax J (2011) Occurrence and fate of organophosphorus flame retardants and plasticizers in coastal and marine surface waters. *Wat Res* 46(2):531–538
- Bradbury SP, Coats JR (1989) Toxicokinetics and toxicodynamics of pyrethroid insecticides in fish. *Environ Tox Chem* 8:373–380
- Broman D, Näf C, Rolff C, Zebühr Y (1991) Occurrence and dynamics of polychlorinated dibenzop-dioxins and dibenzofurans and polycyclic aromatic hydrocarbons in the mixed surface layer of remote coastal and offshore waters of the Baltic. *Environ Sci Technol* 25:1850–1864
- Cantalamesa F (1993) Acute toxicity of two pyrethroids, permethrin and cypermethrin, in neonatal and adult rats. *Arch Toxicol* 67:510–513
- Chen B, Xuan X, Zhu L, Wang J, Gao Y, Yang K, Shen X, Lou B (2004) Distributions of polycyclic aromatic hydrocarbons in surface waters, sediments and soils of Hangzhou City, China. *Wat Res* 38:3558–3568
- Chen H, Liu S, XR X, Liu SS, Zhou GJ, Sun KF, Thao JL, Ying GG (2015) Antibiotics in typical marine aquaculture farms surrounding Hailing Island, South China: occurrence, bioaccumulation and human dietary exposure. *Mar Pollut Bull* 90:181–187
- Coelhan M, Reil I, Rimkus G, Parlar H (2000) Peak patterns of chlorostyrenes in fish and fish oils from the North Atlantic. *Environ Sci Technol* 34:4695–4700
- Craig PJ (1986) Occurrence and pathways of organometallic compounds in the environment – general considerations. In: Craig PF (ed) *Organometallic compounds in the environment*. Longman, Harlow, pp 1–64
- Da Silva BF, Jelic A, Lopez-Serna R, Mozeto AA, Petrovic M, Barcelo D (2011) Occurrence and distribution of pharmaceuticals in surface water, suspended solids and sediments of the Ebro river basin, Spain. *Chemosphere* 85:1331–1339
- Diskowitzky L, Schwarzbauer J (2015) Hexa(methoxymethyl)melamine: an emerging contaminant in German rivers. *Wat Environ Res* 87:461–469
- Diskowitzky L, Schwarzbauer J, Littke R (2002) Distribution of polycyclic musks in water and sediments of the Lippe river (Germany). *Org Geochem* 33:1747–1758
- Diskowitzky L, Schwarzbauer J, Kronimus A, Littke R (2004) The anthropogenic contribution to the organic load of the Lippe river (Germany). Part 2: quantification of specific organic contaminants. *Chemosphere* 57:1288–1293
- Diskowitzky L, Botalova O, Illgut S, Bosowski S, Schwarzbauer J (2015) Identification of characteristic organic contaminants in wastewaters from modern paper production sites and subsequent tracing in a river. *Hazard Mat* 300:254–262
- Diskowitzky L, Sträter M, Dwiytino AF, Irianto HE, Schwarzbauer J (2016) First comprehensive survey of lipophilic organic contaminants in surface waters of the megacity Jakarta, Indonesia. *Mar Pollut Bull* 101:654–664
- Duedahl-Olesen L, Aaslyng M, Meinert L, Christensen T, Jensen AH, Binderup ML (2015) Polycyclic aromatic hydrocarbons (PAH) in Danish barbecued meat. *Food Control* 57:169–176
- Dwiytino DL, Nordhaus I, Andarwulan N, Irianto HE, Lioe HN, Ariyani F, Kleinertz S, Schwarzbauer J (2016) Accumulation patterns of lipophilic organic contaminants in surface sediments and in economic important mussel and fish species from Jakarta Bay, Indonesia. *Mar Pollut Bull* 101:767–777
- Eganhouse RP, Blumfield DL, Kaplan IR (1986) Long-chain alkylbenzenes as molecular tracers for domestic wastes in the marine environment. *Environ Sci Technol* 17:523–530

- Elschenbroich W, Salzer A (1990) Organometallchemie. Teubner Studienbücher, Stuttgart
- Fent K (2013) Ökotoxikologie, 4th edn. Georg Thieme Verlag, Stuttgart
- Franke S, Schwarzbauer J, Francke W (1995) Arylesters of alkylsulfonic acids in sediments. *Fresenius J Anal Chem* 360:580–588
- Frimmel FH, Grenz R, Kordik E, Dietz F (1989) Nitriloacetat (NTA) und Ethylendinitrilotetraacetat (EDTA) in Fließgewässern der Bundesrepublik Deutschland. *Vom Wasser* 72:175–184
- Fritsche W (1998) Umwelt-Mikrobiologie. Gustav Fischer Verlag, Jena
- Fromme H, Schwarzbauer J, Lahrz T, Kraft M, Fembacher L (2017) *Int J Hyg Environ Health* 220:440–444
- Geckeler KE, Eberhardt W (1995) Biogene Organochlorverbindungen – Vorkommen, Funktion, Umweltrelevanz. *Naturwissenschaften* 82:2–11
- Goerlitz DF, Troutman DE, Godsy EM, Franke BJ (1985) Migration of wood-preserving chemicals in contaminated groundwater in a sand aquifer at Pensacola, Florida. *Environ Sci Technol* 19:955–961
- Götz R, Bauer OH, Friesel P, Roch K (1998) Organic trace compounds in the water of the River Elbe near Hamburg part II. *Chemosphere* 36:2103–2118
- Guo J, Chen D, Potter D, Rockne KJ, Sturchio NC, Giesy JP, Li A (2014) Polyhalogenated carbazoles in sediments of lake michigan: a new discovery. *Environ Sci Technol* 48:12807–12815
- Hamscher G, Sczesny S, Höper H, Nau H (2002) Determination of persistent tetracycline residues in soil fertilized with liquid manure by high-performance liquid chromatography with electrospray ionization tandem mass spectrometry. *Anal Chem* 74:1509–1518
- He X, Wang Z, Nie X, Yang Y, Pan D, Leung AOW, Cheng Z, Yang Y, Li K, Chen K (2012) Residues of fluoroquinolones in marine aquaculture environment of the Pearl River Delta, South China. *Environ Geochem Health* 34:323–335
- Heberer T, Gramer S, Stan HJ (1999) Occurrence and distribution of organic contaminants in the aquatic system in Berlin. Part III: determination of synthetic musks in Berlin surface water applying solid-phase microextraction (SPME) and gas chromatography-mass spectrometry (GC-MS). *Acta Hydrochim Hydrobiol* 27:150–156
- Heim S, Ricking M, Schwarzbauer J, Littke R (2005) Halogenated compounds in a dated sediment core of the Teltow Canal, Berlin: time related sediment contamination. *Chemosphere* 61:1427–1438
- Heintz A, Reinhardt G (1991) Chemie und Umwelt, 2nd edn. Friedr. Vieweg/Sohn Verlagsgesellschaft, Braunschweig
- Hirsch R, Ternes T, Haberer K, Kratz KL (1999) Occurrence of antibiotics in the aquatic environment. *Sci Total Environ* 225:109–118
- Howell NL, Suarez MP, Rifai HS, Koenig L (2008) Concentrations of polychlorinated biphenyls (PCBs) in water, sediment, and aquatic biota in the Houston Ship Channel, Texas. *Chemosphere* 70:593–606
- Huerta-Fontela M, Galceran MT, Ventura F (2011) Occurrence and removal of pharmaceuticals and hormones through drinking water treatment. *Wat Res* 45:1431–1442
- Jantzen E (1992) Analytische Untersuchungen zur Beurteilung der Bindungsformen (Species) des Zinns in Elbsedimenten unter Zuhilfenahme von GC-AAS, GC-MS, TRFA und GFAAS. Dissertation Universität Hamburg
- Jantzen E, Kuballa J, Wilken RD (1993) Muster zinnorganischer Verbindungen in der Elbe. *Vom Wasser* 80:245–252
- Järnberg U, Asplund L, de Wit C, Egeback AL, Wideqvist U, Jakobsson E (1997) Distribution of polychlorinated naphthalene congeners in environmental and source-related samples. *Arch Environ Contam Toxicol* 32:232–245
- Kameda Y, Kimura K, Miyazaki M (2011) Occurrence and profiles of organic sun-blocking agents in surface waters and sediments in Japanese rivers and lakes. *Environ Pollut* 159:1570–1576
- Kannan K, Smith RG, Lee RF, Windom HL, Heitmüller PT, Macauley JM, Summers JK (1998) Distribution of total mercury and methyl mercury in water, sediment, and fish from South Florida estuaries. *Arch Environ Contam Toxicol* 34:109–118

- Kasprzyk-Hordern B, Dinsdale RM, Guwy AJ (2008) The occurrence of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs in surface water in South Wales, UK. *Wat Res* 42:3498–3518
- Kim SD, Cho JC, Kim IS, Vanderford BJ, Snyder SA (2007) Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters. *Wat Res* 41:1013–1021
- Kronimus A, Schwarzbauer J, Dsikowitzky L, Heim S, Littke R (2004) Anthropogenic organic contaminants in sediments of the Lippe river, Germany. *Water Res* 38:3473–3483
- Kümmerer K (2001) *Pharmaceuticals in the environment*. Springer, Berlin
- Kwok Z, Franciskovic-Bilinski S, Bilinski H, Branica M (2002) A comparison of anthropogenic mercury pollution in Kastela Bay (Croatia) with pristine estuaries in Öre (Sweden) and Krka (Croatia). *Mar Pollut Bull* 44:1152–1169
- Lalumera GM, Calamari D, Galli P, Castiglioni S, Crosa G, Fanelli R (2004) Preliminary investigation on the environmental occurrence and effects of antibiotics used in aquaculture in Italy. *Chemosphere* 54:661–668
- Law R, Allchin CR, de Boer J, Covaci A, Herzke D, Lepom P, Morris S, Tronczynski J, de Wit CA (2006) Levels and trends of brominated flame retardants in the European environment. *Chemosphere* 64:187–208
- Le TX, Munekage Y (2004) Residues of selected antibiotics in water and mud from shrimp ponds in mangrove areas in Viet Nam. *Mar Pollut Bull* 49:922–929
- Lee HB, Sarafin K, Peart TE, Svoboda ML (2003) Acidic pharmaceuticals in sewage—methodology, stability test, occurrence, and removal from Ontario samples. *Wat Qual Res J Canada* 38:667–682
- Letzel M, Weiss K, Schüssler W, Sengl M (2010) Occurrence and fate of the human pharmaceutical metabolite ritalinic acid in the aquatic system. *Chemosphere* 81:1416–1422
- Li C, Chen J, Wang J, Ma Z, Han P, Luan Y, Lu A (2015) Occurrence of antibiotics in soils and manures from greenhouse vegetable production bases of Beijing, China and an associated risk assessment. *Sci Total Environ* 521–522:101–107
- Lian W, Ren F, Tang L, Dong D (2015) Analysis of polycyclic aromatic hydrocarbons in cigarette samples using gel permeation chromatography clean-up by gas chromatography–tandem mass spectrometry. *Microchem J* 129:194–199
- Lima DRS, Bezerra MLS, Neves EB, Moreira FR (2011) Impact of ammunition and military explosives on human health and the environment. *Rev Environ Health* 26:101–110
- Londono VAG, Reynoso CM, Resnik SL (2015) Polycyclic aromatic hydrocarbons (PAHs) survey on tea (*Camellia sinensis*) commercialized in Argentina. *Food Control* 50:31–37
- Luo Y, Xu L, Wang Y, Zhang H, Alvarez PJJ (2011) Occurrence and transport of tetracycline, sulfonamide, quinolone, and macrolide antibiotics in the Haihe river basin, China. *Environ Sci Technol* 45:1827–1833
- Marotti I, Marotti M, Piccaglia R, Nastri A, Grandi S, Dinelli G (2010) Thiophene occurrence in different *Tagetes* species: agricultural biomasses as sources of biocidal substances. *J Sci Food Agric* 90:1210–1217
- Mason RP, Lawrence AL (1999) Concentration, distribution, and bioavailability of mercury and methylmercury in sediments of Baltimore harbor and Chesapeake Bay, Maryland, USA. *Environ Tox Chem* 18:2438–2447
- Muhaya BBM, Leermakers M, Baeyens W (1997) Total mercury and methylmercury in sediments and in the polychaete *Nereis Diversicolor* at Groot Buitenschoor (Scheldt estuary, Belgium). *Wat Air Soil Pollut* 94:109–123
- Munoz I, Bueno MJM, Agüera A, Fernandez-Alba AR (2010) Environmental and human health risk assessment of organic micro-pollutants occurring in a Spanish marine fish farm. *Environ Pollut* 158:1809–1816
- Naumann K (1993) *Chlorchemie der Natur. Chemie in unserer Zeit* 27:33–41
- O'Neill P (1998) *Chemie der Geo-Bio-Sphäre*. Ferdinand Enke Verlag, Stuttgart

- Oaks JL, Gilbert M, Virani MZ, Watson RT, Meteyer CU, Rideout BA, Shivaprasad HL, Ahmed S, Chaudry MJI, Arshad M, Mahmood S, Ali A, Khan AA (2004) Diclofenac residues as the cause of vulture population decline in Pakistan. *Nature* 427:630–633
- Oikari A, Kukkonen J, Virtanen V (1992) Acute toxicity of chemicals to *Daphnia magna* in humic waters. *Sci Total Environ* 117/118:367–377
- Olsson A, Bergman A (1995) A new persistent contaminant detected in Baltic wildlife: Bis(4-chlorophenyl)sulfone. *Ambio* 24:119–123
- Ostermann A, Siemens J, Welp G, Xue Q, Lin X, Liu X, Amelung W (2013) Leaching of veterinary antibiotics in calcareous Chinese croplands. *Chemosphere* 91:928–934
- Pan G, You C (2010) Sediment–water distribution of perfluorooctane sulfonate (PFOS) in Yangtze River estuary. *Environ Pollut* 158:1363–1366
- Parlar H, Angerhöfer D (1995) *Chemische Ökotoxikologie*, 2nd edn. Springer, Berlin
- Pawelzick HT, Hoper H, Nau H, Hamscher G (2004) A survey of the occurrence of various tetracyclines and sulfamethazine in sandy soils in northwestern Germany fertilized with liquid manure. In: SETAC Euro 14th annual meeting. Prague, Czech Republic, pp 18–22
- Poppe A, Alberti J, Friegle H, Rönnefahrt B (1988) Umweltgefährdung durch chlorierte Diphenylmethane (Ugilec141). *Vom Wasser* 70:33–42
- Poppe A, Alberti J, Bachhausen P (1991) Entwicklung der Belastung nordrhein-westfälischer Flußsedimente mit Tetrachlorbenzyltoluolen und polychlorierten Biphenylen. *Vom Wasser* 76:191–198
- Pouliquen H, Delepee R, Thorin C, Haury J, Larhantec-Verdier M, Morvan ML, Le Bris H (2009) Comparison of water, sediment, and plants for the monitoring of antibiotics: a case study on a river dedicated to fish farming. *Environ Toxicol Chem* 28:496–502
- Quevauviller P, Donard OFX, Wasserman JC, Martin FM, Schneider J (1992) Occurrence of methylated tin and dimethyl mercury in a Mangrove core from Sepetiba Bay, Brazil. *Appl Organometallic Chem* 6:221–228
- Reinecke W, Schlömann M (2007) *Umweltmikrobiologie*. Elsevier – Spektrum Akademischer Verlag, München
- Reiner J, Kannan K (2006) A survey of polycyclic musks in selected household communities from the United States. *Chemosphere* 62:867–873
- Ricking M, Schwarzbauer J, Hellou J, Svenson J, Zitko A (2003) Polycyclic aromatic musk compounds in waste water treatment plant effluents of Canada and Sweden – first results. *Marine Poll Bull* 46:410–417
- Schmidt H, Haapakangas H, van Beelen P (2005) Effects of antibiotics on soil microorganisms: time and nutrients influence pollution-induced community tolerance. *Soil Biol Biochem* 37:1882–1892
- Schulz DE, Petrick G, Duinker JC (1989) Complete characterization of polychlorinated biphenyl congeners in commercial Aroclor and Clophen mixtures by multidimensional gas chromatography-electron capture detection. *Environ Sci Technol* 23:852–859
- Schulze T, Wetterauer B, Schwarzbauer J, Hollert H, Braunbeck T, Ricking M (2003) DDT and Metabolite in Sedimenten Berliner Gewässer: Vorkommen, Analytik und Schädigungspotential. *Umweltwissenschaften und Schadstofforschung UWSF* 15:71–77
- Schwarzbauer J (2005) *Organic contaminants in riverine and groundwater systems*. Springer, Berlin/Heidelberg/New York
- Schwarzbauer J, Heim S (2005) Lipophilic organic contaminants in the Rhine river (Germany). *Wat Res* 39:4735–4748
- Schwarzbauer J, Ricking M, Littke R (2003) DDT-related organic substances bound to particulate matter in sediments of the Teltow Canal, Germany. *Environ Sci Technol* 37:488–495
- Shiraishi H, Pilkington NH, Otsuki A, Fuwa K (1985) Occurrence of chlorinated polynuclear aromatic hydrocarbons in tap water. *Environ Sci Technol* 19:585–590

- Singer H, Müller S, Tixier C, Pillonel L (2002) Triclosan: Occurrence and fate of a widely used biocide in the aquatic environment: field measurements in wastewater treatment plants, surface waters, and lake sediments. *Environ Sci Technol* 36:4998–5004
- Soclo HH, Garrigues P, Ewald M (2000) Origin of Polycyclic Aromatic Hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas. *Mar Pollut Bull* 40:387–396
- Sun J, Luo Q, Wang D, Wang Z (2015) Occurrences of pharmaceuticals in drinking water sources of major river watersheds, China. *Ecotox Environ Safe* 117:132–140
- Taniyasi S, Kannan K, Horii Y, Hanari N, Yamashita N (2003) A survey of perfluorooctane sulfonate and related perfluorinated organic compounds in water, fish, birds, and humans from Japan. *Environ Sci Technol* 37:2634–2639
- Ternes T (1998) Occurrence of drugs in German sewage treatment plants and rivers. *Wat Res* 32:3245–3260
- Ternes TA, Hirsch R (2000) Occurrence and behavior of X-ray contrast media in sewage facilities and the aquatic environment. *Environ Sci Technol* 34:2741–2748
- Thateyus AJ, Selvam ADG (2013) Synthetic pyrethroids: toxicity and biodegradation. *Appl Ecol Environ Sci* 1:33–36
- Tomy GT, Mui DCG, Stern GA, Westmore JB (2000) Levels of C₁₀–C₁₃ polychloro-*n*-alkanes in marine mammals from the arctic and the ST. Lawrence river estuary. *Environ Sci Technol* 34:1615–1619
- Vanderford BJ, Snyder SA (2006) Analysis of pharmaceuticals in water by isotope dilution liquid chromatography/tandem mass spectrometry. *Environ Sci Technol* 40:7312–7320
- Vieno NM, Härkki H, Tuhkanen T, Kronberg L (2007) Occurrence of pharmaceuticals in river water and their elimination in a pilot-scale drinking water treatment plant. *Environ Sci Technol* 41:5077–5084
- Voß V (1997) *Umweltchemie*. Springer, Berlin
- Wang S, Wang H, Deng W (2013) Perfluorooctane sulfonate (PFOS) distribution and effect factors in the water and sediment of the Yellow River Estuary, China. *Environ Monit Assess* 185:8517–8524
- Wester PG, de Boer J (1996) Determination of polychlorinated terphenyls in aquatic biota and sediment with gas chromatography/mass spectrometry using negative chemical ionization. *Environ Sci Technol* 30:473–480
- Xiong W, Sun Y, Zhang T, Ding X, Li Y, Wang M, Zeng Z (2015) Antibiotics, antibiotic resistance genes, and bacterial community composition in fresh water aquaculture environment in China. *Microb Ecol* 70:425–432
- Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S (2002) PAHs in the fraser river basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org Geochem* 33:489–515
- Zamfirescu D, Grathwohl P (2001) Occurrence and attenuation of specific organic compounds in the groundwater plume at a former gasworks site. *J Contam Hydrol* 53:407–427
- Zheng X, Yang Y, Liu M, Yu Y, Zhou JL, Li D (2016) PAH determination based on a rapid and novel gas purge-microsyringe extraction (GP-MSE) technique in road dust of Shanghai, China: characterization, source apportionment, and health risk assessment. *Sci Total Environ* 557–558:688–696
- Zuccato E, Chiabrando C, Castiglioni S, Calamari D, Bagnati R, Schiarea S, Fanelli R (2005) Cocaine in surface waters: a new evidence-based tool to monitor community drug abuse. *Environ Health* 4:14

Further Reading

- Dsikowitzky L, Schwarzbauer J (2014) Industrial organic contaminants: identification, toxicity and fate in the environment. *Environ Chem Lett* 12:371–386
- Gribble GD (2000) The natural production of organobromine compounds. *Environ Sci Pollut Res* 7:37–49
- Hites RA (2011) Dioxins: an overview and history. *Environ Sci Technol* 45:16–20
- Hopkins ZR, Blaney L (2016) An aggregate analysis of personal care products in the environment: identifying the distribution of environmentally-relevant concentrations. *Environ Int* 92-93:301–316
- Li WC (2015) Occurrence, sources, and fate of pharmaceuticals in aquatic environment and soil. *Environ Pollut* 187:193–201
- Young AL, Giesy JP, Jones PD, Newton M (2004) Environmental fate and bioavailability of Agent Orange and its associated dioxin during the Vietnam War. *Environ Sci Pollut Res* 11:359–370

Chapter 3

Petrogenic Contaminations

Outlook

Production and refinement of petroleum results in contamination of the environment as the result of accidents and careless handling. Since petroleum is a complex mixture of compounds, the environmental fate of such petrogenic contaminations is intricate.

Keywords Oil spills • Petroleum products • Crude oil composition • Biodegradation • Water washing

Since industrialization petroleum is one of the most important raw materials. It is explored, produced, transported and refined in enormous amounts for decades. Since the early 1970s the complex contamination by petroleum and its products became more and more obvious, especially due to the environmental damages caused by oil spills as the results of tanker or oil rig accidents (e.g. 1972 *Sea Star* – Gulf of Oman; 1978 *Amoco Cadiz* – Brittany, France; 1989 *Exxon Valdez* – Prince William Sound, Alaska; 2002 *Prestige* – Galicia, Spain; 2010 *Deep Water Horizon* – Gulf of Mexico). However, such accidents are not the only emission sources for oil contaminations. An overview with some rough quantitative estimations for the quantity of emissions towards the marine environment are given in Table 3.1.

Petroleum is a very complex mixture of thousands of compounds that vary depending on the type of petroleum. Commercially, petroleum is refined prior to any application or usage. Common refinement is the distillation under various conditions separating under normal pressure the products gases, benzine and fuel oils. The residue is further distilled under vacuum producing in particular bitumen and lubricating oils (see Fig. 3.1).

For all these distillation fractions, systematic changes of their chemical composition are evident (see Fig. 3.2). The higher the boiling point range the higher the contribution of aromatics and the lower the amount of aliphatic hydrocarbons. In more detail, benzine fuels contain dominantly *n*-, *iso*- and cyclic aliphatics with up

Table 3.1 Estimated discharge of hydrocarbon pollution from various sources towards the marine environment according to published data from US National Research Council, 1985

Contamination source	Emissions (tones per year)
Sea transport	1.070.000
Tanker accident	400.000
Sea exploration accidents	50.000
Refineries and industries on the coastline	300.00
Urban sewage and disposal	820.000
Discharge through rivers	40.000
Illegal oil discharge	20.000
Natural oil sources and sediment erosion	250.000
Rainfall	300.000
Total	3.250.000

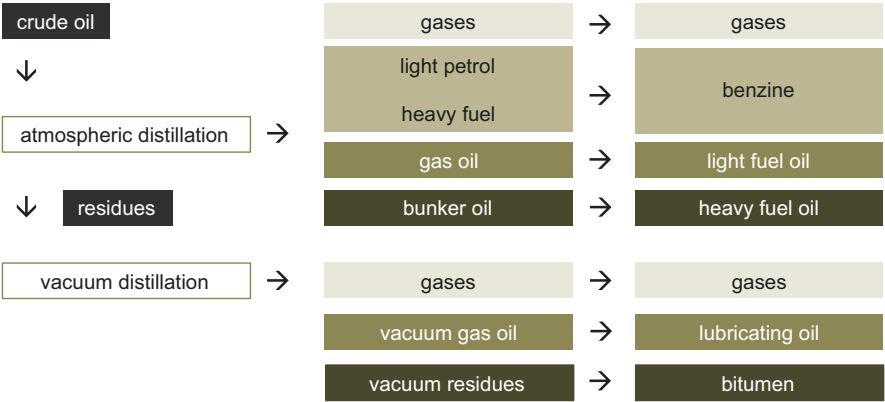


Fig. 3.1 Petroleum refinement and its main products

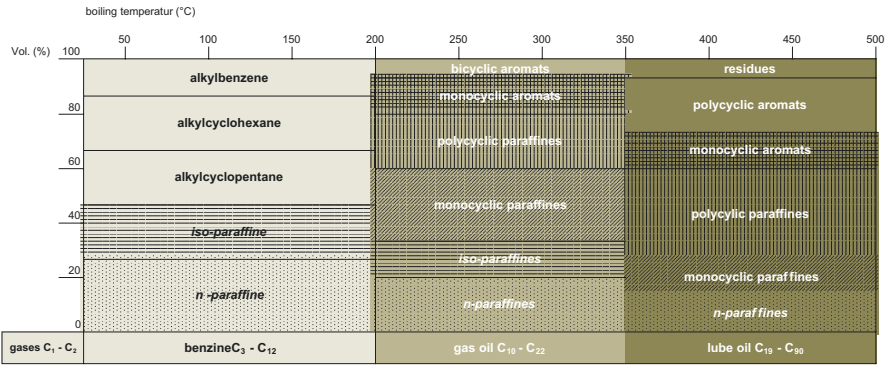


Fig. 3.2 Systematic changes of chemical compositions of the three commercially most important distillation fractions from crude oil

to ca. 90%. They contain only benzene derivatives and no higher aromatics. On the contrary, in lube oils the aromatic fractions account for more than 25%. Also the contribution of cyclic compounds, aliphatic and aromatic, increases with rising boiling point.

The differences in composition are very well visible in gas chromatograms. *n*-Alkanes as significant individual signals are covering different ranges of carbon numbers in kerosene, benzine or diesel fuel. Lube oils on the contrary are characterized by a so-called hump or UCM (unresolved complex mixture) without visible *n*-alkane peaks. Corresponding gas chromatographic analyses are using the pattern of different oil fractions or products to fingerprint elevated contaminations in natural samples such as soils. This is illustrated in Fig. 3.3.

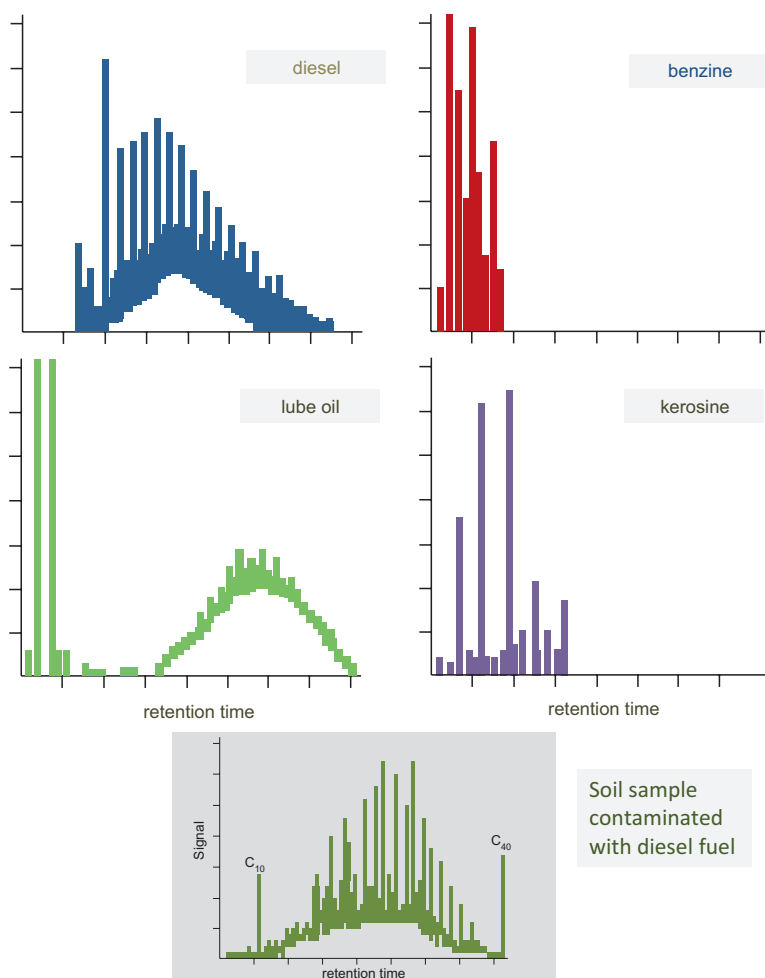


Fig. 3.3 Gas chromatographic pattern of different oil products and a fingerprinting approach for a soil contaminated with diesel fuel

Product yield		Origin		
Fraction	Boiling Range	Brega	Arabian light	Arabian heavy
gases	- 160 - 30°C			
benzines	30 - 180°C			
gas oil	170 - 370°C			
residues	345 - 500°C			

Fig. 3.4 Composition of three different crude oil types according to the resulting distillation fractions

The initial refined products are further treated and converted for final products. E.g. the various types of fuels are processed by chemical conversion of raw oil distillation fractions with higher boiling point and accordingly more long chain alkanes. The conversion processes especially for shortening the higher molecular weight components are *inter alia* thermal and hydrous cracking as well as various forms of catalytic cracking or platforming. These processes are necessary, since the commercial needs (e.g. the demand on fuels in relation to bunker oil) do not fit with the petroleum consistence and the related quantities of distillation fractions. Additionally, the compositions of the crude oils differ according to their origin. Variations of their principal components according to the resulting distillation fractions for different crude oils are exemplified in Fig. 3.4. It is obvious, that the quality of the crude oil determines significantly the yield of individual distillation fractions.

Noteworthy, raw, refined and fine products are subject to discharge towards the environment to various extents. Knowledge about the composition of petroleum products at all levels of production are essential to assess a petrogenic contamination correctly. These variations of composition have huge effects of the environmental assessment of corresponding contaminations.

Beside the molecular aspects, the processes, by which petrogenic emissions are exposed, have to be differentiated for both emission scenarios and polluted compartments. Beside the already mentioned emission towards the marine environment, the discharge of oil and oil products to soils is a common environmental problem.

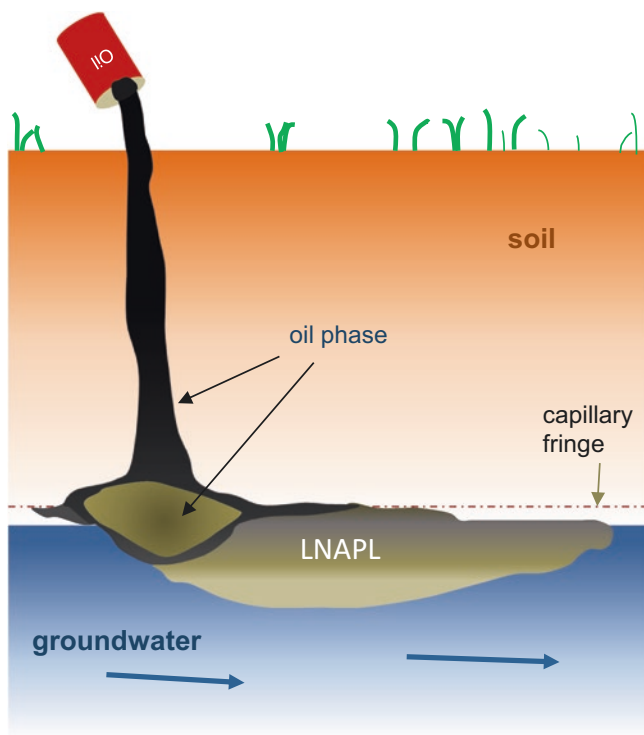


Fig. 3.5 Scheme of environmental dispersion of oil type contamination in soil / ground water systems

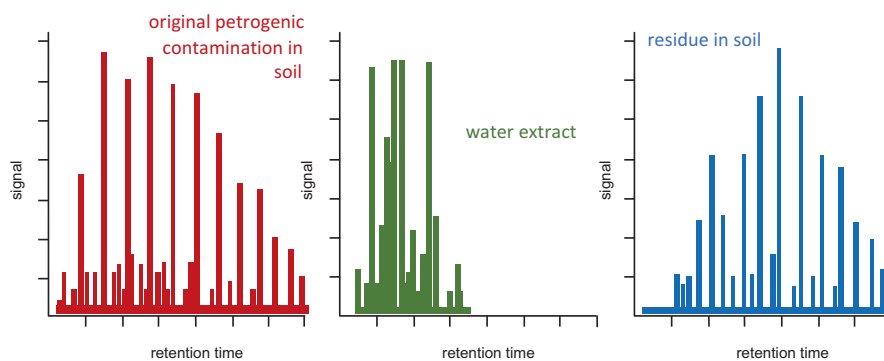
Oil dispersion in soil systems is similar to the scenario described for PER in Fig. 2.7. Oil seeps through the unsaturated zone as a plume, where low volatile proportions of the oil residue can be volatilized. Once reaching the groundwater systems, oil forms a so-called light non-aqueous phase liquid or LNAPL due to its mainly lower density compared to water (see Fig. 3.5). Here a separation of low and high dense oil fractions can partly be observed over longer time periods.

In both soil and marine environments oil type pollutants face aerobic and anaerobic conditions. Due to the complex mixture of substances in oil and oil products as well as the heterogeneous environmental conditions and the diverse environmental processes (as summarized in Table 3.2), the long-term behavior of petrogenic pollution is intricate.

However, some general trends and changes in composition in particular on the molecular level are reported. These processes affect the principal groups of oil constituents. A process observable also in natural systems (e.g. oil reservoirs) is water washing, that represents the partial dissolution of more water-soluble compounds from the oil plume at the water-oil interface. A depletion of low molecular weight components as well as functionalized substances becomes obvious in the water washed residues. This is exemplified for main components in Fig. 3.6.

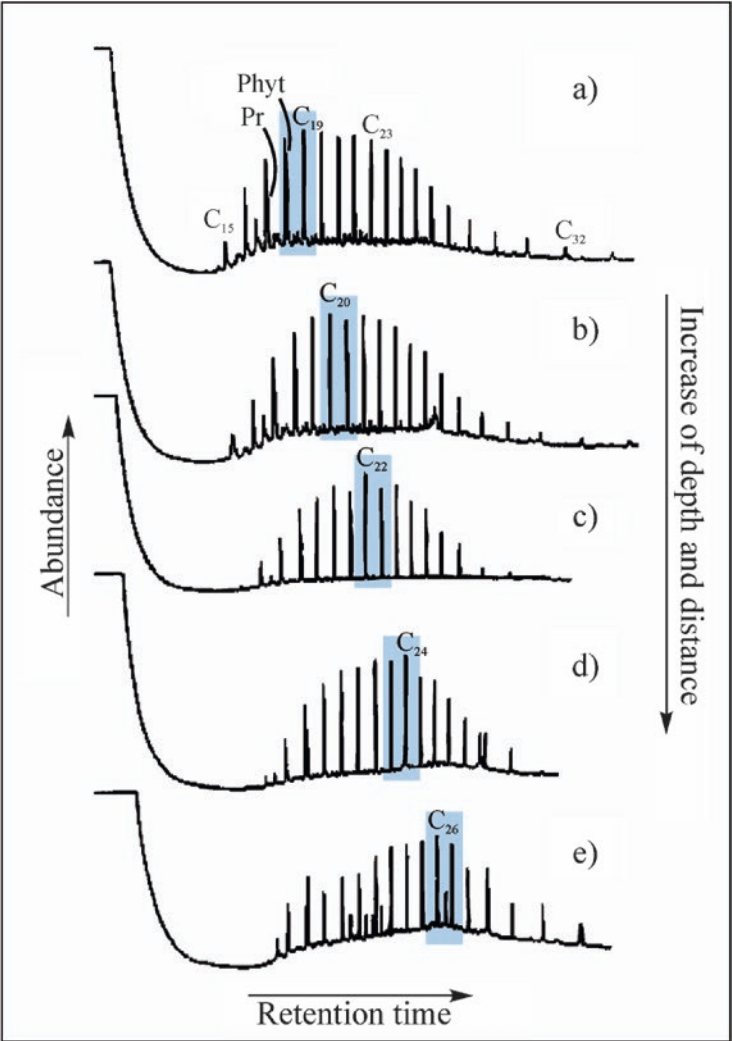
Table 3.2 A brief summary of transfer, transport and transformation processes that oil type contaminations are subject to in various environmental compartments

Environment compartment	Interaction of oil type pollutants
Surface water	Adsorption on and precipitation with suspended particles, emulsion, dispersion, aerobic biodegradation, water washing
Aquatic sediments, soils	Adsorption, slow migration, aerobic/anaerobic biodegradation
Ground water	Adsorption, dispersion, anaerobic bioodegradation, water washing
Atmosphere	Evaporation, photooxidation

**Fig. 3.6** Effect of water washing of an oil contamination. Changes are visible in the gas chromatograms of oil contamination, water extract and residue

A similar effect is known for the evaporation of oil pollution from soil towards the atmosphere. Here, the oil residues become depleted in low volatile components.

A further process affecting the composition of oil contaminants is related to their tendency to migrate through the environmental compartments (e.g. soils or sediments). The interaction of the various, chemically different constituents with the particulate phase (mainly adsorption and desorption), the interaction with water as well as the formation of and transport in micelles lead to systematic depletion of more interacting fractions. This phenomenon can also be called ‘geo-chromatography’ and is illustrated in Fig. 3.7 where the composition of a petroleum pollution is monitored directly at an oil spill and at four locations in different distances. The corresponding gas chromatograms illustrate a shift towards longer *n*-alkanes with distance pointing to a transport by colloidal micelles. However, looking at the principal relative composition of aliphatics, aromatics and so-called NSO components (representing the more polar compounds exhibiting functional groups with nitrogen, sulphur or oxygen) a higher mobility of the more polar fractions are obvious for the longest distance.



Sample	Aliphatics (%)	Aromatics (%)	NSO-fraction (%)
At the oil spill (a)	28	43	12
b	28	49	17
c	29	48	19
d	30	47	15
e	16	24	47

Fig. 3.7 Changes in the composition of an oil contamination with distance from the oil spill as pointed out by gas chromatograms and principal components (Modified after Jovančičević et al. 1996)

The most important process with impact on oil pollution is the microbial degradation. Principal degradation pathways of the most important ingredients of oils, aliphatic and aromatic hydrocarbons are already described in Sect. 1.3. These transformation reactions appear on different time scales. Less resistant compounds degrade faster as the more recalcitrant. This leads to a general shift of oil composition affected by biodegradation.

An example is given in Fig. 3.8 (adapted from Jovančičević et al. 2001). Here, the biodegradation of an oil contamination in a groundwater system has been observed for nearly two years. The presented gas chromatograms show a clear depletion of *n*-alkanes in the course of biodegradation. The branched alkanes (represented by the terpenoic biomarker compounds phytane and pristane) persist for a longer time period but start to diminish after several months as well. The relation of pristane and phytane to their nearby eluting *n*-alkanes, *n*-C₁₇ and *n*-C₁₈ respectively, is a parameter describing the progress of biodegradation (see the table in Fig. 3.8). The parameter increases with time for the upper well but remains more or less stable in the lower well. These differences point to a slower degradation rate in the lower and more anaerobic part of the ground water system.

With the same approach different degradation rates can be observed also for aromatic compounds and alicyclic hydrocarbons. A rough order of degradation is: *n*-alkanes > branched alkanes > alicyclic hydrocarbons > aromatic hydrocarbons. These observations have been used to quantitatively categorize the extent of biodegradation. Two systems are given in Table 3.3a,b. Basically, the disappearance of individual compounds or substance groups is the key parameter for ranking the different biodegradation levels.

General Note

Petrogenic contaminations are a complex mixture of substances with a high structural diversity. Their environmental fate after emission is influenced by several parameters changing the composition of the oil pollutants partly in systematic way. The systematic changes can be used to obtain information about the environmental processes (e.g. biodegradation, water washing etc.).

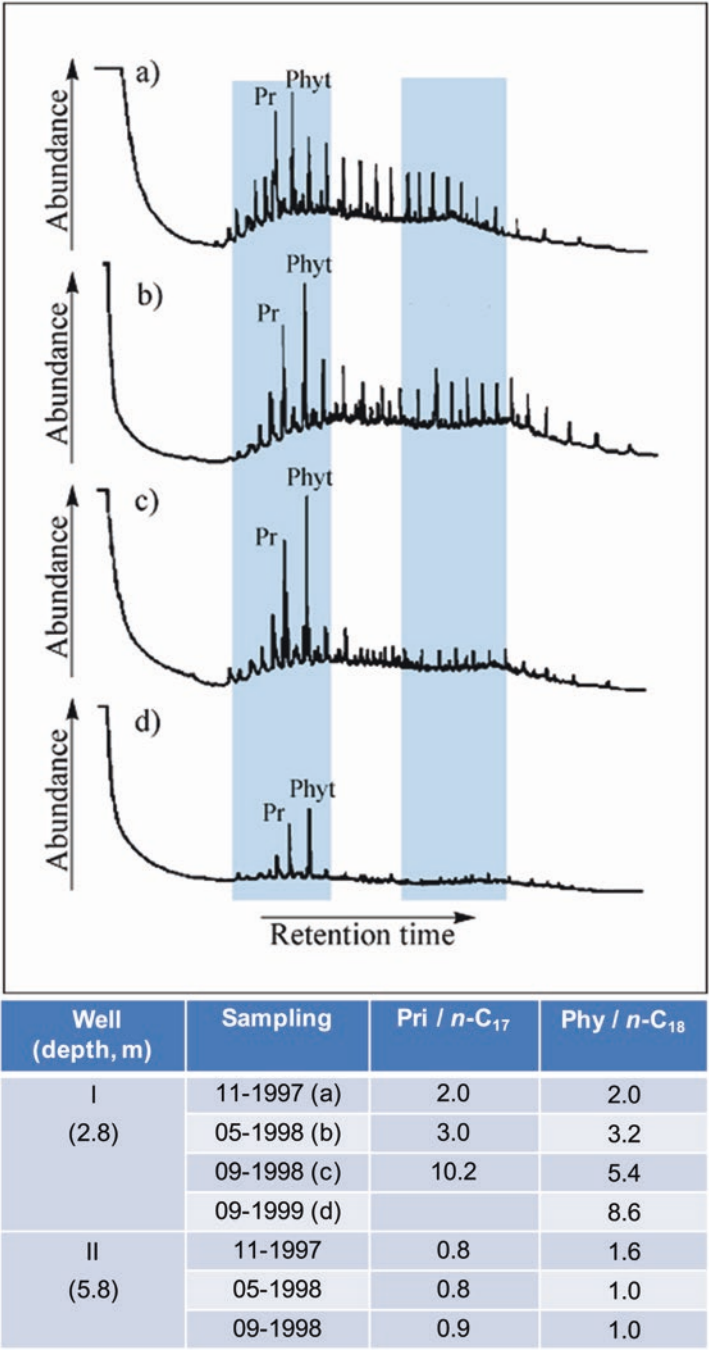


Fig. 3.8 Systematic shifts of oil pollutant composition induced by biodegradation (Modified after Jovančičević et al. 2001). The gas chromatograms as well as the corresponding parameters in the table demonstrate the depletion of *n*-alkanes with time and a correlated more persistent behavior of isoprenoids (pristane and phytane)

Table 3.3a 9-Level classification of biodegraded oils according to Volkman et al. (1983)

Level	Removed hydrocarbons	Degree of biodegradation
1	No	–
2	The lower n-alkanes	Minimum
3	More than 99% of n-alkanes	Moderate (I)
4	Alkylcyclohexanes, partly isoprenoids	Moderate (II)
5	All isoprenoids	Moderate (III)
6	Bicyclic alkanes	Medium strong
7	More than 50% of regular steranes	Strong
8	Steranes changed, appearance of a lot of demethylated hopanes	Very strong
9	All regular steranes, dominance of diasteranes and demethylated hopanes	The maximum

Table 3.3b 6-Level classification of biodegraded oils according to Head et al. (2003)

Level	Initial removal of specific hydrocarbons	Degree of biodegradation
1	No	None
2	Propane, <i>n</i> -alkanes, <i>iso</i> -alkanes,	Very slight
3	Butane, pentanes, C ₆ -C ₁₅ isoprenoid alkanes, naphthalenes	Slight
4	Ethane, isobutane, alkylcyclohexanes, C ₁₅ -C ₃₅ isoprenoid alkanes, phenanthrenes, dibenzothiophenes	Moderate
5	Chrysenes, alkylcarbazoles, regular steranes	Heavy
6	Hopanes, triaromatic steroids, monoaromatic steroids, gammacerane, oleanane, C ₂₁ -C ₂₂ steranes, tricyclic terpanes, diasteranes,	Severe

Excursus – Biodegradation experiments on oil type pollutants

It is difficult to study exclusively the process of biodegradation in nature. The superimposition of all the other processes already mentioned (water washing, evaporation, adsorption etc.) hinders an unambiguous identification of the effects of biodegradation on the molecular composition of oil type pollutants. Therefore, much information on oil biodegradation derived from laboratory experiment with selected microorganism directly applied to petrogenic pollutants. Here, a clear trend for many substance groups is evident as demonstrated in the figures below for an incubation experiment with zymogenoeus microorganisms. The gas chromatograms point to a rapid degradation of *n*-alkanes (a), a clear resistance of hopanes and steranes as well as a preferred degradation of unsubstituted aromatics as compared to their alkylated derivatives (note: methylated aromatics are also faster degraded than the C₂-derivatives).

(continued)

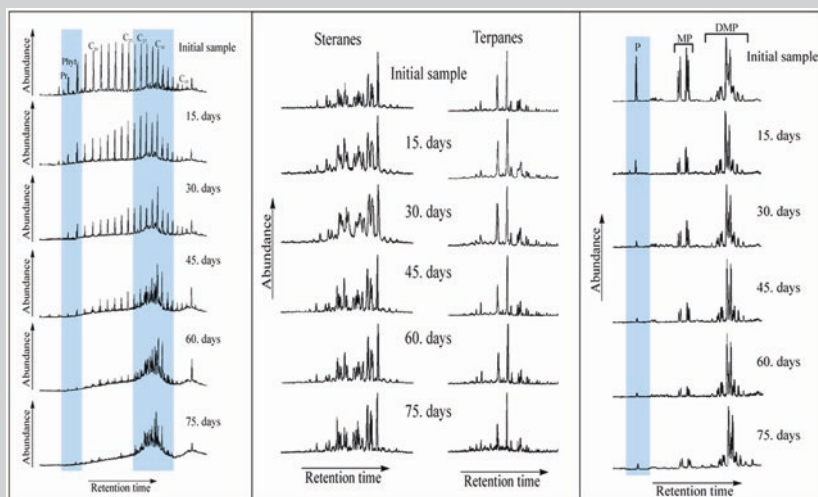


Figure: Gas chromatograms of *n*-alkanes, hopanes and steranes as well as phenanthrene and its alkylated homologues during the time course of an incubation experiment representing the time related changes of oil constituents during biodegradation (Novaković et al. 2012)

References

- Head IM, Jones DM, Larter S (2003) Biological activity in the deep subsurface and the origin of heavy oil. *Nature* 426:108–112
- Jovančičević B, Lj T, Vujasinović S, Matić I, Malović D, Pfendt P (1996) A contribution to the elucidation of oil migration mechanisms through water-wet sediments: crushed rock environment as example. *J Serb Chem Soc* 61:1025–1031
- Jovančičević B, Polić P, Vitorović D, Scheeder G, Teschner M, Wehner H (2001) Biodegradation of oil-type pollutants in Danube alluvial sediments (Yugoslavia). *Fresenius Environ Bull* 10:178–182
- Novaković M, Ramadan MMA, Šolević Knudsen T, Antić M, Beškoski V, Gojgić-Cvijović G, Vrvic MM, Jovančičević B (2012) Degradation of methyl-phenanthrene isomers during bioremediation of soil contaminated by residual fuel oil. *Environ Chem Lett* 10:287–294
- Volkman JK, Alexander R, Kagi RI, Woodhouse GW (1983) Desmethylated hopanes in crude oils and their application in petroleum geochemistry. *Geochim Cosmochim Acta* 47:785–794

Further Reading

- Kaplan IR, Galperin Y, ST L, Lee RP (1997) Forensic environmental geochemistry: differentiation of fuel-types, their sources and release time. *Org Geochem* 27:289–317

Chapter 4

POPs – A Special Perspective on a Specific Group of Contaminants

Outlook

One group of environmental contaminants received high attention during the last decades due to their high environmental stability, the so-called *persistent organic pollutants* or POPs. Here, this group of pollutants and its linkage with the *Stockholm Convention* are briefly discussed.

Keywords Dirty dozen • Stockholm convention • Persistence • Halogenated pollutants • Ban

As described in detail in Chap. 2, the number and amount of harmful chemicals used and discharged by human beings is very high. In environmental discussions one group of contaminants attracts a specific and high attention, the Persistent Organic Pollutants (POPs). As indicated by their name, POPs are long-lasting chemicals due to their large resistance to decomposition processes resulting in a high persistence. In addition, POPs are usually remarkable (eco)toxic and exhibit a distinct lipophilicity becoming apparent in a very low water solubility (see also Chap. 1). As a result of these properties two environmentally important implications are evident for POPs. Firstly, they tend to bioaccumulate primarily in fatty tissues of organisms including humans. Here, the accumulation along the food chain is an important environmental pathway. First evidence for the negative impact of chemicals on ecosystems aroused firstly for typical POPs. Well known are studies from the 50s pointing to DDT contamination as main reason for observed thinning of eggshells causing an extensive decline of wild bird populations in UK and USA.

Secondly, these chemicals are easily transported over long distances. For example, a general and global transport from warmer Earth regions to colder areas (e.g. arctic regions) as the result of continuous volatilization and deposition (also associated with dust particles) has been observed.

Due to these environmental highly relevant properties and harmful effects, POPs have been investigated intensively over decades. Special focus was laid on those

Table 4.1 Summary of some global regulations for protecting the environment by reducing or even eliminating relevant pollutants

Act	Year of adoption and initiation	Task
Montreal protocol	1987/1990	Measures to prevent depletion of stratospheric ozone layer caused by anthropogenic emissions
Kyoto protocol	1997/2005	Convention on reducing anthropogenic emissions of greenhouse gases, in particular CO ₂ . Measures to reduce global warming.
Rotterdam convention	1998/2004	Regulations for hazardous chemicals by global control and management of hazardous substances and waste, as well as the control of transboundary movements. Similar to the “Basel Convention” from 1989 (put into effect on May 5th 1992).
Aarhus convention	1998/2001	Access to information, public participation, and access to justice in the field of environmental protection

POPs that occur ubiquitous and at higher concentrations. As a further parameter, the observed environmental impairments induced by POPs were motivation not only for intensive scientific research but also for being implemented in political and legal actions.

Regarding POPs the so-called *Stockholm Convention* is a milestone in acting politically for reducing and ban of harmful pollutants. This convention is a part of a series of acts, protocols or conventions aiming at reducing the global pollution level (see Table 4.1).

The *Stockholm Convention* addressing the Persistent Organic Pollutants was adopted in the capital of Sweden on May 22nd 2001. It was put into effect on May 17th 2004 when it was ratified by 50 countries. The goal of this convention is to limit and ban the production, use, i.e. emissions, and trade of POPs. It originally covered 12 chemicals in three annexes. Here, by definition, chemicals are pure chemical compounds, derivatives or their mixtures. Annex A covers compounds that should be completely eliminated, annex B contains a list of substances that should be restricted but not totally banned, and annex C comprises compounds that were unintentionally produced making it difficult to prevent their emission. Two substances or substance groups, which belong to two categories (PCBs and HCB), are listed in annexes A and C. These first twelve compounds are also known as the *dirty dozen* and are illustrated in Fig. 4.1. Principally they can be divided in pesticides and chlorinated aromatics technically produced or formed unintentionally during technical or related processes. However, most of these compounds are already discussed in Chap. 2. Based on the *Stockholm Convention* huge efforts have been started for detection and monitoring of these preselected POPs (see e.g. Xu et al. 2013).

The ban of POPs in the frame of the *Stockholm Convention* is a dynamic process. In recent years, the annexes have been expanded by several substances and substance groups exhibiting similar environmental stability and impact on ecosystems as the Dirty Dozen. From 2009 to 2015 ten new substances or substance groups

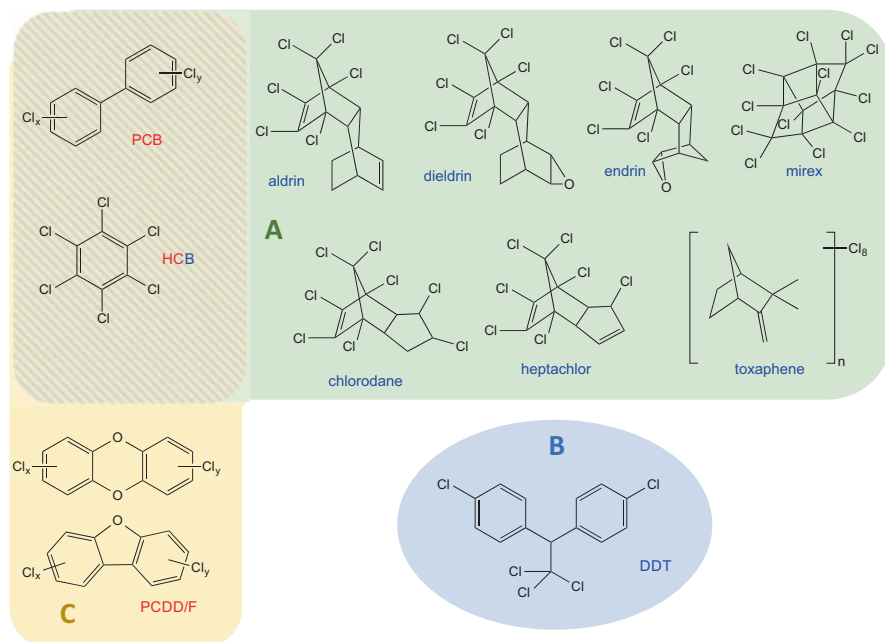


Fig. 4.1 The *Dirty Dozen*. Letters and colored areas indicate the *Stockholm Convention* annexes, in which the compounds are listed. Substances named in blue are pesticides, names in red point to chlorinated aromatics

have been added dominantly to annex A comprising further chlorinated and brominated substances. Only one compound has been categorized as restricted pollutant (annex B), which is noteworthy the only fluorinated contaminant, PFOS. More structural details are summarized in Fig. 4.2.

General Note

All substances appearing in the annexes of the *Stockholm Convention* are halogenated compounds. In addition to the *Dirty Dozen*, which are all chlorinated compounds, brominated and fluorinated substances have been added in the current annexes as well. Here, a close relation between halogenation and persistence becomes obvious.

It has to be noted, that certainly also the *Stockholm Convention* faces critical statements and objections. The classifications, in particular as mentioned for annex A, are not as strict as they seem to be. There are several exceptions that prevent a complete ban of some POPs. For example, lindane is allowed yet to be used as human pharmaceutical against head lice and scabies. And also DDT is still legally in use in numerous tropical countries as effective agent against Malaria disease.

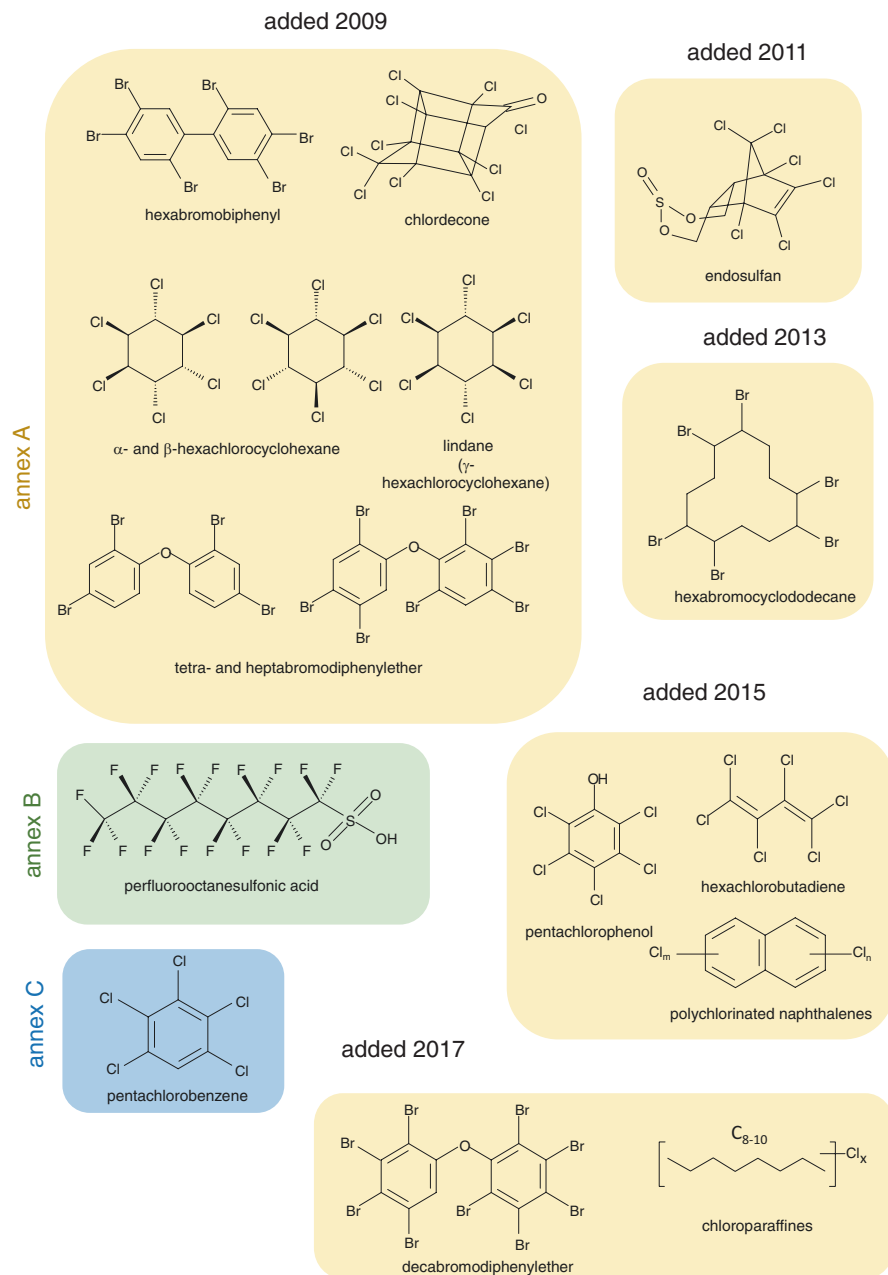


Fig. 4.2 Molecular structures of pollutants added to annexes A, B and C of the *Stockholm Convention* following the *Dirty Dozen*

Excursion – Remediation of POP contamination – a huge challenge

When their adverse effects on the environment and on wildlife was assessed, high interest was spent to find a way to destroy POPs, i.e. to remediate polluted environmental compartments. Remediation of PCB-contaminated waste in Japan (Osaka PCB waste treatment facility, see Fig. below) is a very good example for the huge effort that is needed to decontaminate PCB containing material (such as transformer or capacitor oils) in a sustainable way. In a first step, PCBs are tried to be separated from surrounding materials e.g. by extraction procedures. Following, the PCB containing extracts (partly diluted with paraffinic solvents) are subjected to a dechlorination treatment at 260 °C under pressure and in the presence of hydrogen as well as a Pd/C type catalyst. This dechlorination process forms hydrochloric acid that can be easily washed out. The reaction products (biphenyl and related derivatives) are subjected to further decomposition treatment. The catalyst and excess hydrogen can be recycled.

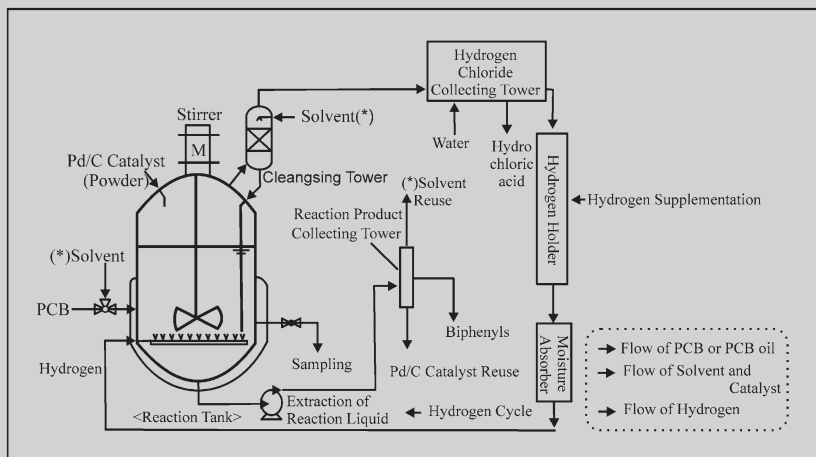


Figure: Schematic diagram of a technical PCB degradation procedure. (The authors express gratitude to Japan Environmental Safety Corporation, JESCO, for permission to show the treatment pathway at Osaka PCB Waste Treatment Facility)

Reference

Xu W, Wang X, Cai Z (2013) Analytical chemistry of the persistent organic pollutants identified in the Stockholm Convention: a review. *Anal Chim Acta* 790:1–13

Chapter 5

Anthropogenic Marker

Outlook

Organic contaminants obtain scientific attention not only due to harmful effects but also because of their indicative properties. Indicative are the molecular structures with high emission source specificity. Anthropogenic marker can be used to trace the anthropogenic impact on ecosystems in time and space.

Keywords LABs • I/E ratio • Urobilin • Fecal steroids • 2-(4-morpholinyl) benzothiazol

In most cases of environmental geochemical studies the focus lies on the emission, fate and effects of harmful pollutants. Basic motivation is to identify the environmental risk of anthropogenic emissions. However, not only organic pollutants but also organic contaminants with no or minor harmful effects are targets of environmental analyses due to their indicative properties. Here, the correlation of molecular structure and source specificity are the clue to use such indicators for tracing the anthropogenic impact on ecosystems. This approach is closely related to the biomarker concept (see also Vol. 2 of this series – From Biomolecules to Geofossils, Chap. 2), consequently, the application of indicative organic substances for environmental questions is often called *anthropogenic marker* approach (see Fig. 5.1). Basics have been developed and described by Robert P. Eganhouse and Hideshige Takada (Takada and Eganhouse 1998).

Primary preconditions for using organics as anthropogenic marker are (i) a reasonable amount emitted more or less continuously to the environment, (ii) an enhanced environmental stability and, as already mentioned, (iii) an unambiguous allocation of substance and emission source. One further prerequisite is an easy analytical handling.

Noteworthy, the implementation of the anthropogenic marker approach is limited so far. On the one hand, it has been applied more or less exclusively to the aquatic ecosystems. Here, the water phase and the particulate matter have to be

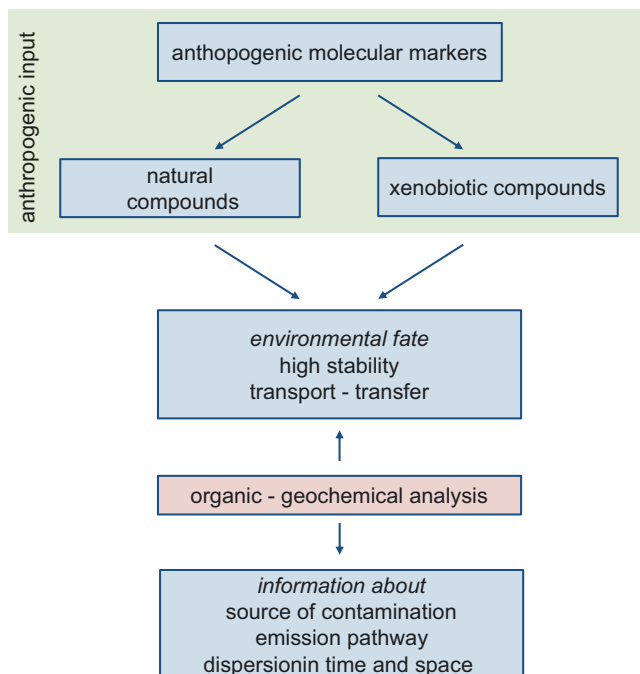


Fig. 5.1 Basic scheme of the anthropogenic marker approach (Modified from Takada et al. 1997)

distinguished. In water samples, hydrophilic marker compounds are suitable tracers, whereas in particulate matter more lipophilic compounds have to be used. On the other hand, the anthropogenic marker approach has traced dominantly effluents from municipal sewage systems as emission sources so far. Two groups of markers can be distinguished, natural compounds and synthetic compounds, both specifically emitted by anthropogenic effluents. Natural markers comprise e.g. caffeine or tocopherylacetate, a food additive derived from vitamin E. Synthetic compounds indicating municipal effluents belong dominantly to the group of detergents and their derivatives such as nonylphenols, dialkyltetraline sulfonates or alkylbenzenesulfonic acid based substances. A brief summary of common lipophilic and hydrophilic anthropogenic markers used so far as well as their emission sources are given in Fig. 5.2.

As a good example for source specificity is the emission of urobilin. The biogenic origin of urobilin is haem as part of the blood pigment haemoglobin. Its unique porphyrin based structure remains more or less preserved during the initial metabolism steps in human bodies comprising the formation of bilirubin in the liver by ring cleavage and the former transformation to urobilinogen by intestinal bacteria (see Fig. 5.3). Once released to the environment by excretion, urobilin is formed by oxidation processes, which is environmentally stable enough to act as an anthropogenic marker and to indicate fecal emissions. Here, the structural similarity of the

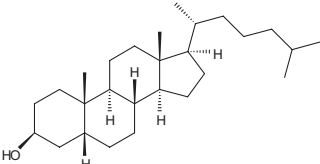
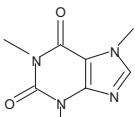
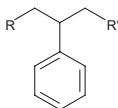
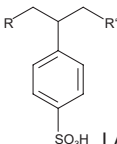
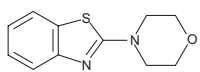
Source		Hydrophobic Markers (Sediment/Suspended matter)	Hydrophilic Markers (Water)
Municipal sewage	Natural substances	 Coprostanol/coprostanone	 Caffeine
		α - Tocopherylacetate	Urobilin
	Synthetic detergents	 LAB	 LAS
		TAB	ABS
		Trialkylamins	Dialkyltetraline sulfonates
		Nonylphenols	
Urban runoff		 4-(2-Morpholinyl)benzothiazol	

Fig. 5.2 Classification of common anthropogenic markers with respect to their application in water or sediment samples and their emission sources (Simplified after Takada et al. 1997)

original biomolecule with the marker compound as well as the knowledge about its transformation in humans allows its application as unambiguous indicator.

A further example for a similar specific source characterization comprises steroid metabolites. Cholesterol (cholesterine) is an ubiquitous constituent in cell membranes of a huge proportion of organisms. The initial metabolism step in organisms is the hydration of the double bond at 5-position (see Fig. 5.4). This leads to two different stereoisomers cholestanol and coprostanol, since the bridging carbon atom becomes a stereo center. Common metabolites are cholestanol and, following, cholestanone for the major proportions of organism. However, intestinal bacteria in humans convert cholesterol to the stereoisomer coprostanol and following coprostanone. Only a few other species like sheeps produce also a significant proportion of this conversion product (see Fig. 5.4). Steroids and their metabolites are excreted with feces and coprostanol is used as human fecal indicator. Typical ratios of these indicators in samples known to be contaminated by human feces are illustrated in

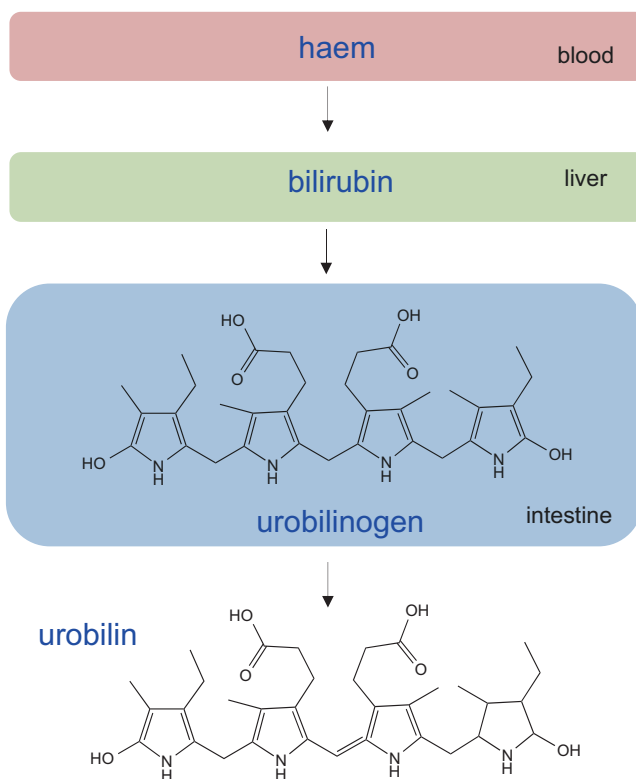


Fig. 5.3 Transformation pathway of the biomolecule haem to urobilin as anthropogenic marker compound

Fig. 5.5. Additionally, some values for fecal steroids measured in surface water sediments from the urban area of Jakarta are given in Fig. 5.6 pointing to the huge emission of untreated sewage effluents.

Beside natural indicators, mainly synthetic compounds are useful anthropogenic marker. The most prominent anthropogenic marker are the linear alkylbenzenes, LABs. They have been already introduced as precursor and residues of the detergents LAS (see Sect. 2.4). Consequently, they are typical constituents of household effluents and characterize the municipal sewage discharge. LAS can act as water related biomarker, but LABs are widespread used as sedimentary anthropogenic marker. A good example how anthropogenic marker can describe the emission and distribution characteristics of municipal effluent is located at the Bay of Tokyo. The LAB concentration profile demonstrates the huge emission from urban sewage towards the coastal environment (Fig. 5.7).

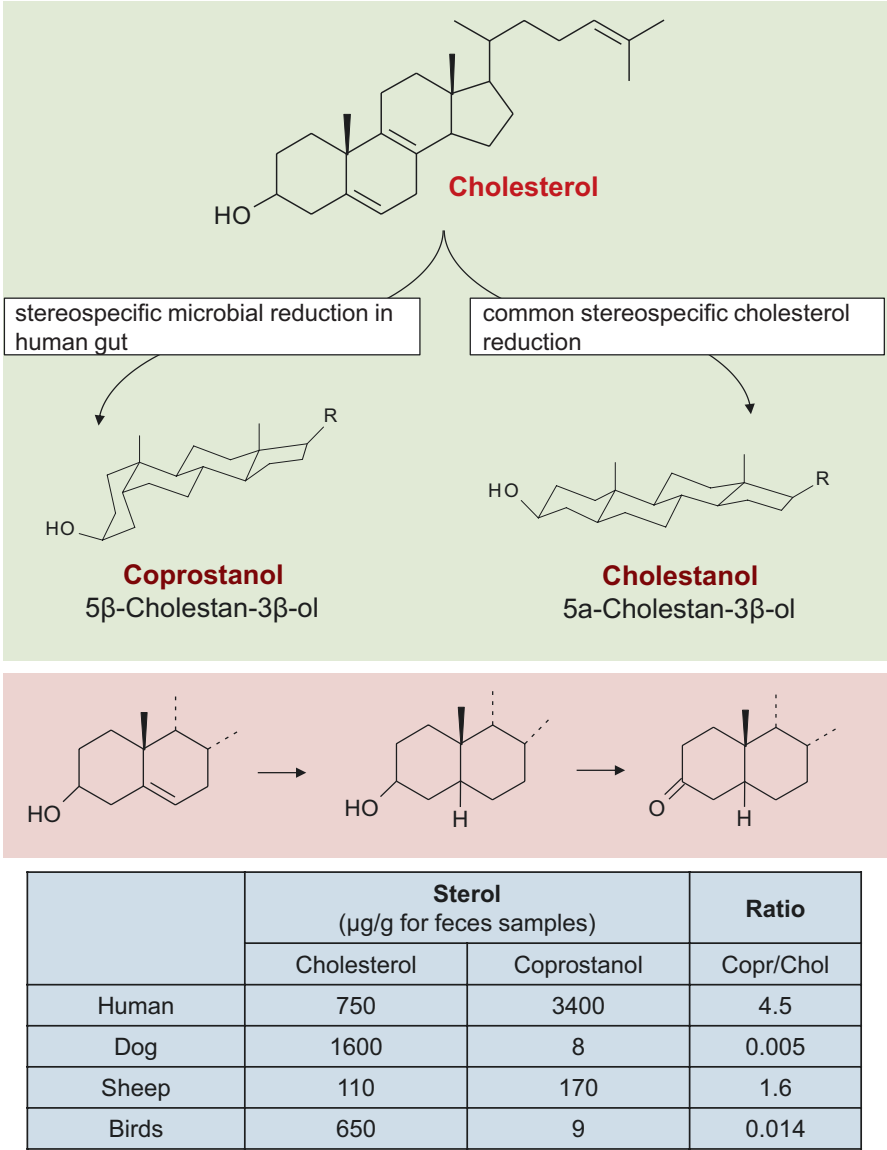


Fig. 5.4 Two pathways of initial metabolization of cholesterol forming two different stereoisomers, either cholestanol or coprostanol (upper part). Further transformation processes lead to cholestanone or coprostanone (middle part). Measured fecal sterol contents in feces of different organisms are given in the lower part (Data adapted from Leeming et al. 1996)

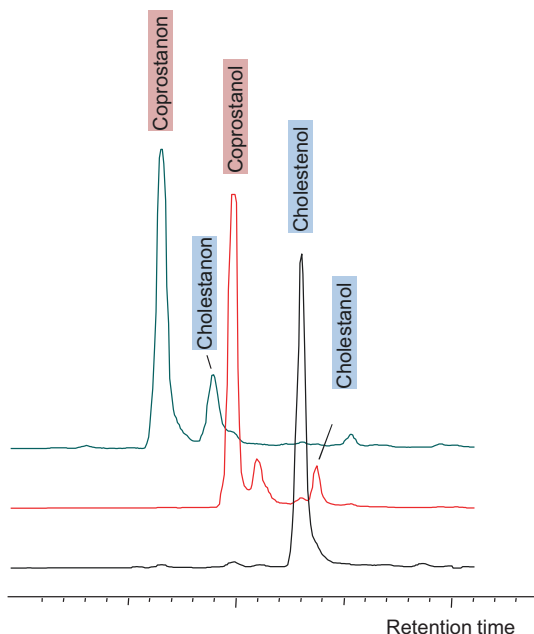


Fig. 5.5 Gas chromatographic elution pattern of steroids in a sediment sample obviously contaminated by fecal emissions

Excursion – The gas chromatographic pattern of LABs

LABs are analyzed mainly by gas chromatography coupled to mass spectrometry, GC/MS. Here, the gas chromatographic pattern of LABs is very specific and allows a fast identification of these compounds in natural samples, e.g. river sediments. LABs pattern is a superimposition of homologues series and individual substitution isomers within each homologue group. Homologues elute nearly equidistant but the individual isomers with increasing retention time distances. This resulting pattern is clearly visible in gas chromatographic analyses and a finger-print for technical LABs mixtures allowing an unambiguous identification of LAB contamination in natural samples such as sediments.

(continued)

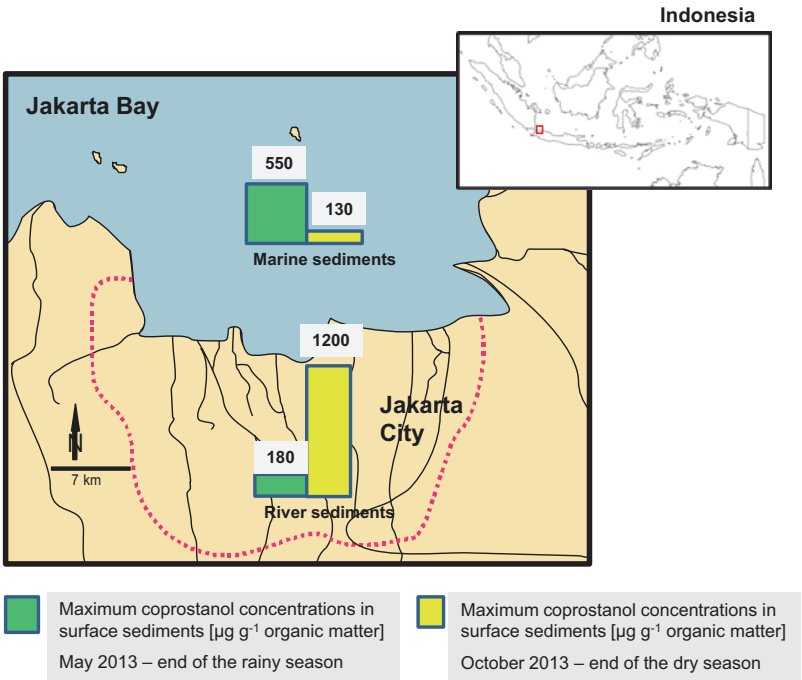
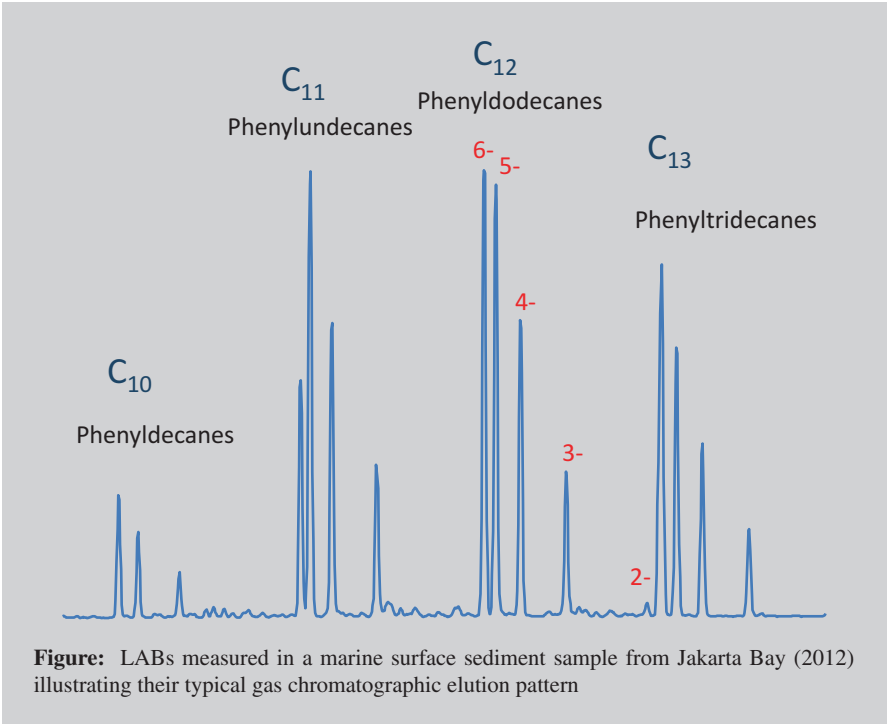


Fig. 5.6 Distribution and quantity of fecal steroid derivatives in sediments of Jakarta and Jakarta Bay (unpublished results)

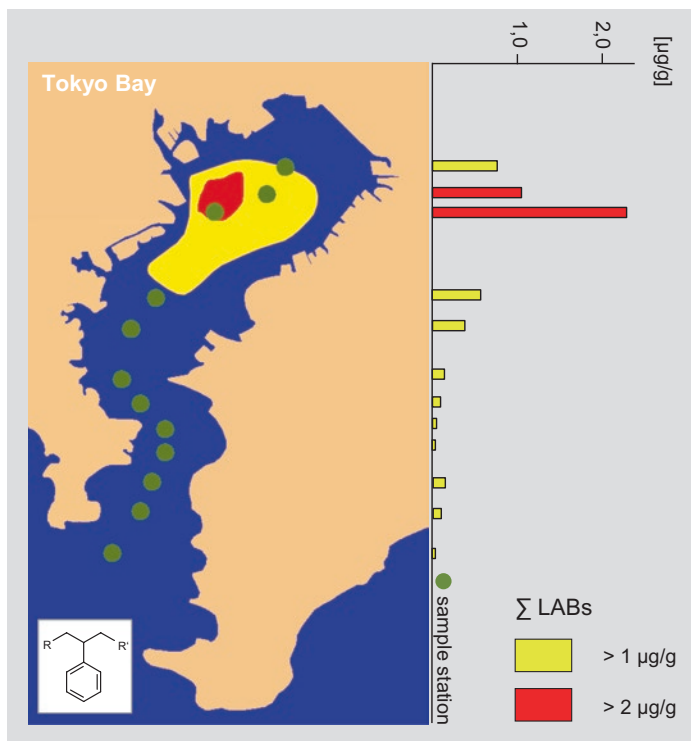


Fig. 5.7 LAB concentrations measured in Tokyo Bay (Modified after Takada et al. 1997 and citations therein)

Beside the source specificity, LAB analyses also gain insight into degradation rates. Systematic incubation experiments under aerobic conditions point to a different degradation rate for individual LAB positional isomers. The compounds with the phenyl substitution in the outer positions (e.g. 1-, 2- or 3- position) tend to be degraded faster as compared to the more internal substituted isomers (4-,5- or 6- position). This varying degradation rates can be used to follow the degree of degradation as illustrated in Fig. 5.8. The ratio of internal versus external substituted isomers, the so-called I/E-ratio, rises with increasing degradation rate. Commonly, for this calculation the very prominent dodecylbenzenes are used. An impact of the different degradation rates is visible clearly in the isomer pattern as visible in gas chromatograms. Here, a shift from an equal distribution of individual isomers to a pattern with decreasing intensities towards the later eluting, internal substitution isomers at higher degradation levels is visible.

Further on, LAB analyses represent also a powerful tool to follow the usage of detergents and, consequently, the emission of domestic sewage not only in space but also in time. A good example is the substitution ABS by LAS during the 60s for improving the biotic degradation potential of detergents. This process is also visible in appropriate sedimentary archives tracing the concentration profiles of their side products TABs and LABs (see also Sect. 2.4) as pointed out in Fig. 5.9.

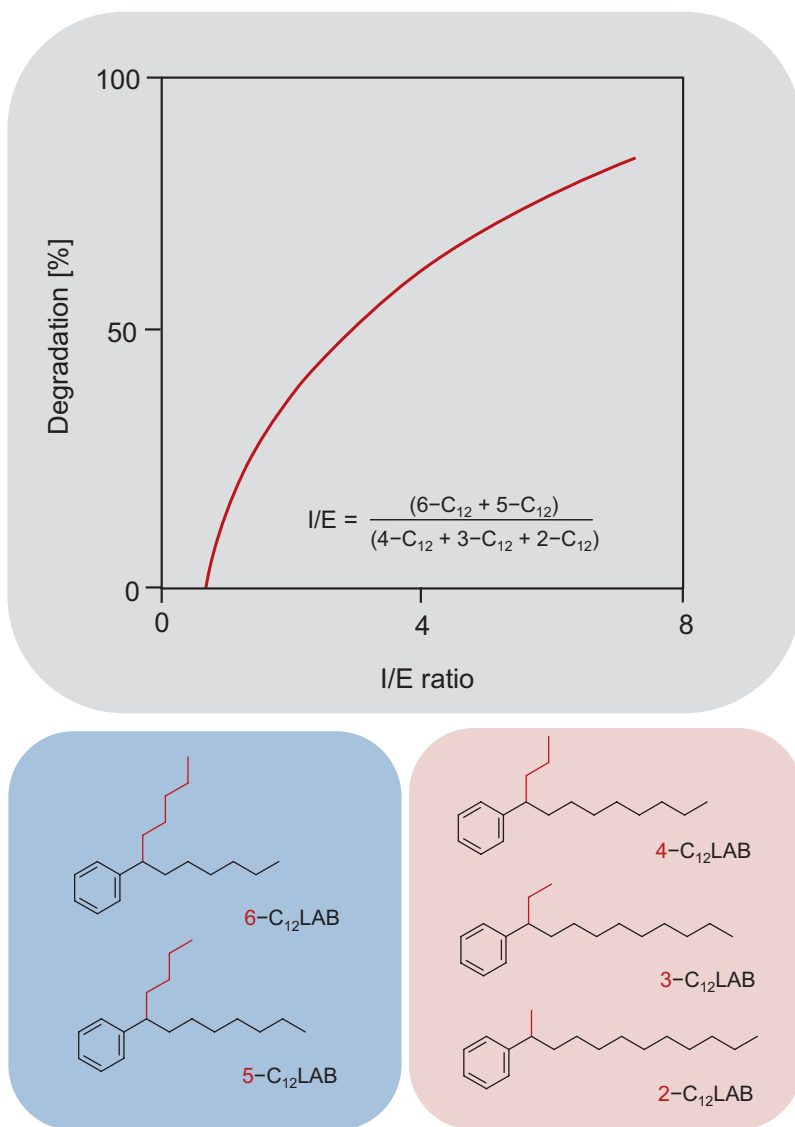


Fig. 5.8 Systematic changes of I/E ratio correlated with degradation rate in an incubation experiment with sewage (Modified after Takada et al. 1997)

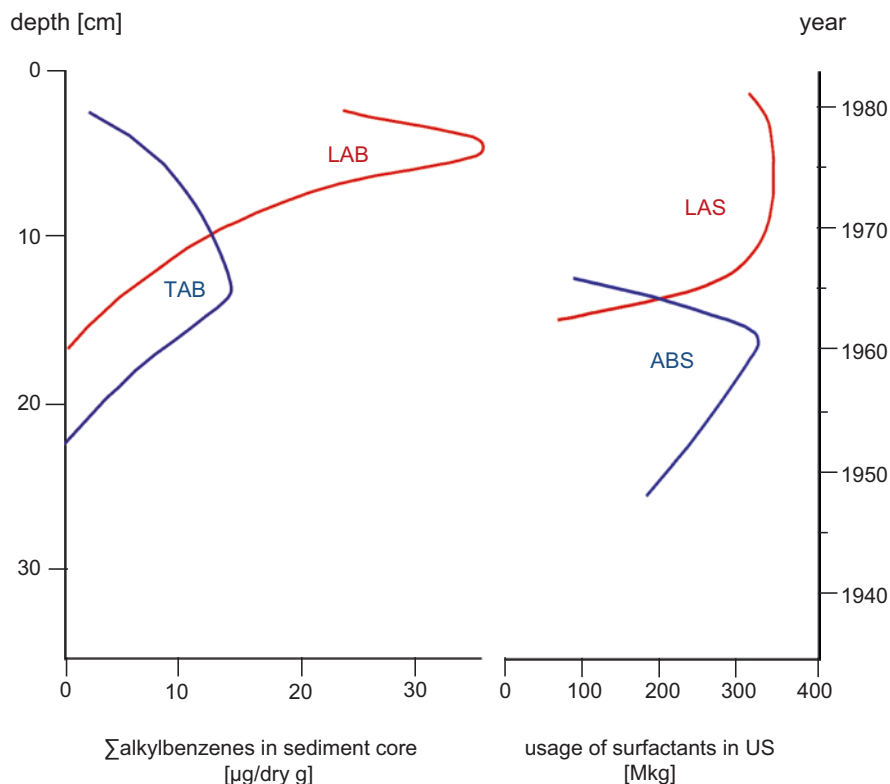


Fig. 5.9 Correlation of LABs detected in a marine sedimentary archive and production rates in US. The substitution of ABS by LAS is clearly visible in the geochronological concentration profiles of TAB and LAB (Compiled and simplified after Eganhouse et al. 1986)

As a last example, the application of anthropogenic marker for tracing the spatial dispersion is also well illustrated by a study performed in the Bay of San Francisco using 2-(4-morpholinyl)benzothiazol (see Fig. 5.10). This substance is intensively used as vulcanization accelerator in rubber synthesis. It remains in the rubber products and is therefore also a constituent in rubber tires. Abrasion of tire rubber during car driving is the main emission source for this benzothiazol derivative. Hence, its occurrence can be attributed to street run-off, basically urban street run-off, and, consequently, 2-(4-morpholinyl)benzothiazol acts as anthropogenic marker for street or urban run-off. Keeping this indicative property in mind, the environmental data obtained for sediments along a transect in the San Francisco Bay clearly point to the influence of an urban area.

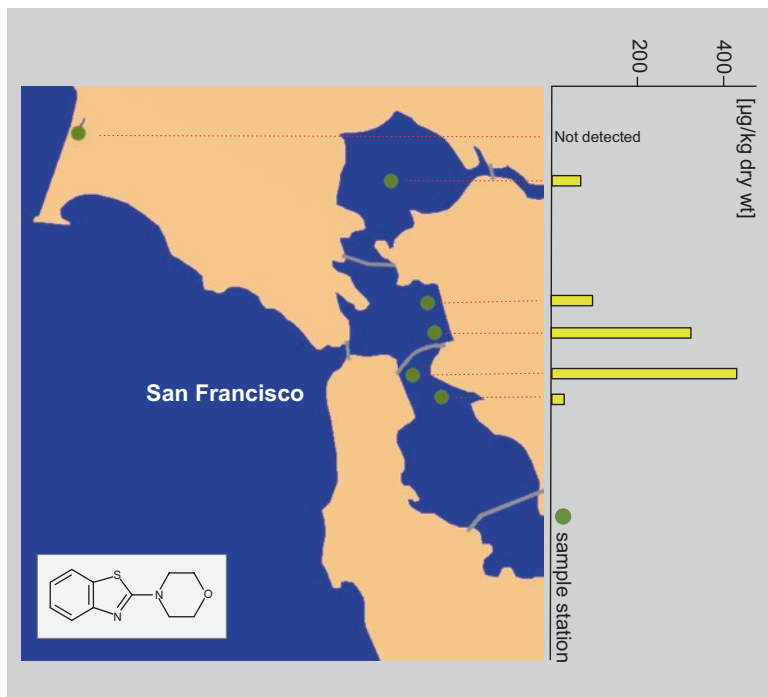


Fig. 5.10 2-(4-Morpholinyl)benzothiazol concentrations in sediments from San Francisco Bay (Adapted from Spies et al. 1987). The concentration profile characterizes the influence from the urban area of San Francisco/Oakland

References

- Eganhouse RP (1986) Long-chain alkylbenzenes: their analytical chemistry, environmental occurrence and fate. *Int J Environ Anal Chem* 26:241–263
- Leeming R, Ball A, Ashbolt N, Nichols P (1996) Using faecal sterols from humans and animals to distinguish faecal pollution in receiving waters. *Water Res* 30:2893–2900
- Spies RB, Andresen BD, Rice DW (1987) Benzothiazoles in estuarine sediments as indicators of street runoff. *Nature* 327:697–699
- Takada H, Eganhouse RP (1998) Molecular markers of anthropogenic waste. In: Meyers RA (ed) *Encyclopedia of environmental analysis and remediation*. Wiley, New York, pp 2883–2940
- Takada H, Futoshi S, Bothner MH, Tripp BW, Johnson CG, Farrington JW (1997) Anthropogenic molecular markers: tools to identify the sources and transport pathways of pollutants. In: *Molecular markers in environmental geochemistry*, ACS Symposium Series 671, Washington, DC, pp 178–195

Further Reading

- Eganhouse RP (1997) Molecular markers and environmental organic geochemistry: an overview.
In: Eganhouse RP (ed) Molecular markers in environmental geochemistry. ACS Symposium
Series 671, Washington, DC, pp 1–21
- Eganhouse RP (2004) Molecular markers and their use in environmental organic geochemistry.
Geochem Invest Earth Space Sci 9:143–157
- Harwood JJ (2014) Molecular markers for identifying municipal, domestic and agricultural
sources of organic matter in natural waters. Chemosphere 95:3–8